Supporting information

"Metal-Templated Ligand Architectures for Trinuclear Chemistry: Tricopper Complexes and Their O_2 Reactivity"

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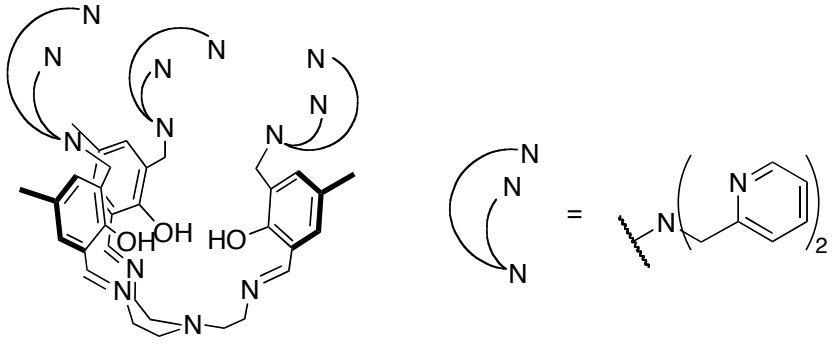
Experimental Details

General considerations.

All procedures were carried out using standard Schlenk techniques or in a M. Braun glovebox filled with purified nitrogen unless stated otherwise. All reactions involving metal reagents were carried out in the glovebox. Anhydrous THF was purchased from Aldrich in 18 L Pure-Pac™ containers. Anhydrous dichloromethane, acetonitrile, diethyl ether, and THF were purified by sparging vigorously with nitrogen for 15 minutes and then passing under nitrogen pressure through a column of activated A2 alumina (Zapp's). Anhydrous DMF was purchased from Sigma-Aldrich and stored under nitrogen over 4 Å molecular sieves. Spectrophotometric grade acetone was purchased from Sigma-Aldrich, dried over calcium sulfate, vacuum-transferred onto additional calcium sulfate, vacuum-transferred a second time, and stored in the glovebox. Propionitrile was purchased from Sigma-Aldrich and dried over CaH_2. All non-dried solvents used were reagent grade or better. All NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. NMR solvents were dried as follows: CD_3CN and CD_2Cl_2 over calcium hydride, C_6D_6 over sodium benzophenone ketyl. All NMR solvents were degassed by three freeze-pump-thaw cycles and vacuum-transferred prior to use. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 300 MHz instrument or on a Varian 400 MHz instrument, with shifts reported relative to TMS as determined by observation of the residual solvent peak. Unless otherwise noted, all commercially available materials were used as received. $Y(CH_2SiMe_3)_3(THF)_2$ and all $Ln(SiMe_3)_3$ salts were prepared according to published procedures.[1,2] UV-Vis spectra were collected on a Varian 50Bio spectrophotometer using a Schlenk-adapted 1 cm quartz cuvette. Low-temperature UV-Vis spectra were obtained using a Varian dip-probe (661.202-UV, 10 mm) and a custom-made glass vessel.

Synthesis of 2.

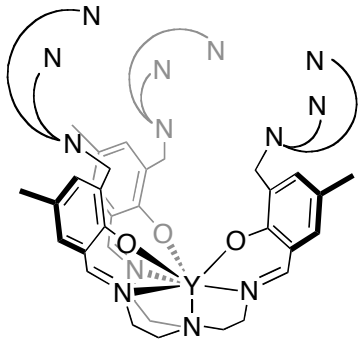


2

In a Schlenk tube, aldehyde **1** (0.617 g, 1.78 mmol)[3] and tris(2-aminoethyl)amine (0.088 mL, 0.592 mmol, 0.33 equiv) were added against positive nitrogen pressure. Dry methanol (15 mL) was added via cannula transfer and the reaction was stirred at room temperature for 16 hours. Volatile materials were removed under vacuum to yield the product as a yellow powder (91%). ^1H-NMR (300 MHz, C_6D_6): δ 14.08 (s, 3H, ArO*H*), 8.43 (s, 6H, Ar*H*), 7.69 (s, 3H, ArC*H*NCH_2), 7.62 (m, 6H, Ar*H*), 7.55 (br s, 6H, Ar*H*),

7.13 (m, 6H, Ar*H*), 6.58 (m, 6H, Ar*H*), 5.75 (s, 3H, Ar*H*), 4.12 (s, 6H, NCH_2Ar) 4.10 (s, 12H, NCH_2Ar), 3.02 (br s, 6H, NCH_2CH_2N), 2.19 (br s, 6H, NCH$_2$CH_2N), 2.09 (s, 9H, CH_3Ar) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2): δ 166.18 (Ar*C*HN), 160.21 (Ar), 157.63 (Ar), 148.96 (Ar), 135.43 (Ar), 133.90 (Ar), 130.62 (Ar), 126.52 (Ar), 126.04 (Ar), 122.23 (Ar), 121.28 (Ar), 118.33 (Ar), 60.06 (N*C*H$_2$Ar), 57.99 (N*C*H$_2$Ar), 55.79 (NCH$_2$*C*H$_2$N), 51.96 (N*C*H$_2$CH$_2$N), 20.22 (Ar*C*H$_3$) ppm. HRMS (FAB), $C_{69}H_{76}N_{13}O_3$: calculated m/z = 1134.619; observed m/z = 1134.6188 (M+H$^+$).

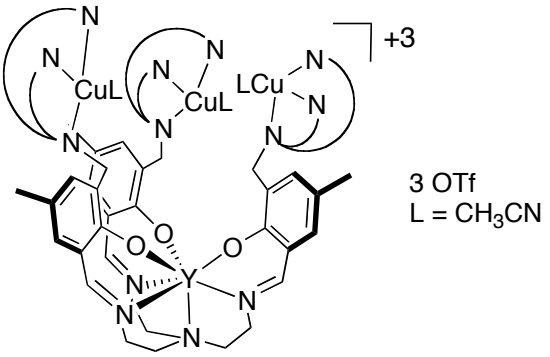
Synthesis of 3.



3

In a 20 mL scintillation vial, **2** (0.0538 g, 0.047 mmol) was dissolved in THF (5 mL) and the solution frozen in a cold well. A solution in THF (3 mL) of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.0235 g, 0.047 mmol, 1 equiv) was also frozen in the cold well. The thawing yttrium alkyl solution was added dropwise to the thawing ligand solution. The reaction mixture was stirred at room temperature for 4 h, during which time it turned from yellow to green to green-blue. The volatile materials were removed *in vacuo* to give a greenish solid. The solid was washed with hexane, diethyl ether, benzene, and THF. The THF filtrate was collected and evaporated to give 0.037 g of yttrium complex product as a yellow powder (64%). ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 8.38 (s, 6H, *o*-Py*H*), 7.98 (s, 3H, ArC*H*NCH$_2$), 7.48 (m, 6H, Py*H*), 7.38 (m, 6H, Py*H*), 7.09 (d, 2.4 Hz, 3H, Ar*H*), 7.02 (m, 6H, Py*H*), 6.60 (d, 2.4 Hz, 3H, Ar*H*), 4.13 (m, 3H, ArC*H*H'N), 3.56 (m, 15H, NCH_2Ar+NCH_2CH_2N), 3.28 (m, 3H, NCH*H'*Ar), 3.17 (m, 3H, NC*H*H'Ar), 2.99 (m, 6H, NCH_2Ar), 2.14 (s, 9H, CH_3Ar) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2): δ 167.95 (Ar*C*HN), 164.33 (Ar), 161.06 (Ar), 148.43 (Ar), 136.47 (Ar), 135.62 (Ar), 132.77 (Ar), 128.15 (Ar), 122.76 (Ar), 121.37 (Ar), 121.09 (Ar), 120.81 (Ar), 59.86 (N*C*H$_2$Ar), 59.30 (N*C*H$_2$Ar), 57.96 (NCH$_2$*C*H$_2$N), 52.08 (N*C*H$_2$CH$_2$N), 20.11 (Ar*C*H$_3$) ppm. HRMS (FAB), $C_{69}H_{76}N_{13}O_3Y$: calculated m/z = 1220.502; observed m/z = 1220.505 (M+H$^+$).

Synthesis of 4.



4

Yttrium complex **3** (0.2189 g, 0.179 mmol) was suspended in CH_3CN (4 mL). A solution of $Cu(CH_3CN)_4OTf$ (0.2028 g, 0.538 mmol, 3 equiv) in THF (3 mL) was added dropwise. The solution turned from cloudy and yellow to clear and golden. The solution was filtered through Celite and the solvent removed *in vacuo* to yield the yttrium-tricopper complex **4** in near-quantitative yield. ^{1}H-NMR (300 MHz, CD_3CN): δ 8.45 (s, 6H, *o*-Py*H*), 8.23 (s, 3H, ArC*H*NCH_2), 7.77 (m, 6H, Py*H*), 7.38 (m, 6H, Py*H*), 7.08 (d, 2.4 Hz, 3H, Ar*H*), 7.00 (m, 6H, Py*H*), 6.79 (d, 2.4 Hz, 3H, Ar*H*), 4.32 (m, 3H, ArC*H*H'N), 3.98 (m, 3H, NCH*H'*Ar), 3.51 (m, 18H, NCH_2Ar+NCH_2CH_2N), 2.94 (m, 6H, NCH_2Ar), 2.05 (s, 9H, CH_3Ar) ppm. ^{13}C-NMR (101 MHz, CD_3CN): δ 167.73 (Ar*C*HN), 164.03 (Ar), 157.40 (Ar), 148.64 (Ar), 138.23 (Ar), 137.70 (Ar), 134.50 (Ar), 125.41 (Ar), 123.74 (Ar), 123.41 (Ar), 121.74 (Ar), 120.69 (Ar), 58.65 (NCH_2Ar), 57.59 (NCH_2CH_2N), 54.39 (NCH_2Ar), 19.34 (ArCH_3) ppm. Elemental analysis: Calculated for $C_{78}H_{81}Cu_3F_9N_{16}O_{12}S_3Y$: C 47.28, H 4.12, N 11.31. Found: C 46.93, H 4.00, N 11.02.

Synthesis of 5

Compound **5** was prepared *in situ* in a UV-Vis vessel equipped with a fiber-optic dip probe for low temperature studies. A solution of complex **4** in propionitrile, 1:1 toluene/acetonitrile, or 3:2 toluene/acetonitrile (~0.2mM) was prepared in a glovebox and 12 mL were added to the UV-Vis cell. The dip probe setup was sealed and taken out on the benchtop, where the cell was cooled to -78°C (propionitrile) or -40°C (toluene/acetonitrile). A small portion of the same solvent was saturated with dioxygen on a Schlenk line by vigorous bubbling for a few minutes, after which 2mL of said solution were added to the UV-Vis cell via syringe. Formation of **5** was complete instantaneously (-40°C) or in about 1 minute (-78°C). Identification of **5** via mass spectroscopy (ESI) was unsuccessful.

λ_{max}, nm (ε, $M^{-1}cm^{-1}$): 355 (12,400), 480 (1,910), 640 (800).

Volumetric measurement of O_2 consumption

To determine the stoichiometry of the reaction between **4** and O_2, a solution of **4** in acetonitrile was degassed via three freeze-pump-thaw cycles on a high-vacuum line. While the solution was still frozen, a known amount of O_2 (~10 equiv) was measured with a volumetric Schlenk bulb and added to the reaction vessel. The reaction solution

was warmed to -40ºC and stirred for one hour, during which the solution changed in color from yellow to dark brown. The solution was again frozen using a dry-ice/acetone bath (-78ºC), and the gas present in the headspace was measured with a Toepler pump.[4] Three freeze-pump-thaw cycles were carried out on the final reaction solution to recover all unreacted gases. Table 1 summarizes the results of three separate runs of volumetric measurements. Per equivalent of **4**, 0.97 ± 0.01 equivalents of O_2 were consumed.

#	mmol **4**	T (K)	O_2 added (mmHg)	mol O_2 added	Final O_2 (mmHg)	Final O_2 (mmol)	mmol O_2 consumed	Equiv consumed
1	0.0413	295	220.5	0.3955	216.0	0.3560	0.0395	0.97
2	0.0353	295	191.0	0.3426	187.5	0.3090	0.0336	0.95
3	0.0436	293	200.0	0.3612	192.0	0.3186	0.0426	0.98

Table S1. Results of volumetric O_2 measurements. Volumetric bulb volume = 33.0 mL, Toepler pump volume = 30.32 mL.

Determination of H_2O_2 release by Ti(IV)oxysulfate titration

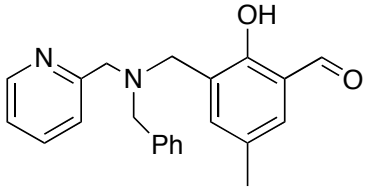
To determine whether species **5** is a peroxide complex, a solution of **5** prepared as described above was treated with formic acid (5 equiv), after which a solution of Ti(IV)oxysulfate was added. The absence of increased absorbance at 408 nm indicated that no H_2O_2 was released within the limits of detection.[5,6]

Reactions of 5 with substrates

Reactivity of **5** with substrates was first investigated under UV-Vis conditions to monitor the decay of **5**. Species **5** was formed as described above at -78ºC; the desired reagent was solubilized in 1 mL of reaction solvent in the glovebox and added to the UV-Vis dip probe vessel via syringe. The reaction was monitored via UV-Vis spectroscopy; reaction was deemed to occur when bands corresponding to **5** decreased by more than 15%.
For certain substrates (phenols, PPh_3, thiophenols, *p*-methylbenzylalcohol) reactivity with **5** was also studied at larger scale to isolate and identify reaction products. In these cases, **5** was prepared by exposure of a solution of **4** in acetonitrile/toluene to excess O_2 on a Schlenk line at -40ºC. Excess O_2 was removed by three freeze-pump-thaw cycles, and the desired substrate added as an acetonitrile/toluene solution under inert atmosphere. The solution was then stirred at -40ºC until disappearance of the dark orange/brown color indicative of **5**. The solution was then warmed to room temperature and the solvent removed *in vacuo*. The reaction vessel was returned to a glovebox where the residue was studied under inert atmosphere with the appropriate spectroscopic techniques.

Reaction with triphenylphosphine was worked up by extraction of the dried reaction mixture with diethyl ether and the product was quantified by integration of its ^{31}P-NMR spectroscopy against excess triphenylphosphine starting material.
Reaction with TEMPO-H was monitored by UV-Vis spectroscopy and the product (TEMPO radical) was quantified by EPR spectroscopy (see spectrum below), and comparison to an authentic sample of TEMPO$^{\bullet}$.
Reaction with 4-*tert*-butylthiophenol was worked up by extraction of the dried reaction mixture with diethyl ether and the product was quantified by NMR spectroscopy.
Thiophenol-bound complex **4**•$(ArSH)_3$ was synthesized by addition of thiophenol to **4** and analysis by ^{1}H- and ^{13}C-NMR spectroscopy, elemental analysis, and ESI-MS
^{1}H-NMR (400 MHz, CD_3CN): δ 8.96 (br s, 6H, SAr*H*), *8*.49 (s, 6H, *o*-Py*H*), 8.27 (s, 3H, ArC*H*NCH_2), 7.76 (m, 6H, Py*H*), 7.46 (m, 2H, SAr*H*), 7.36 (m, 6H, Py*H*), 7.07 (s, 3H, Ar*H*), 7.05 (m, 6H, Py*H*), 6.86 (s, 3H, Ar*H*), 4.48-4.32 (m, 6H, NCH_2), 4.03-3.64 (m, 18H, NCH_2), 3.31 (m, 3H, NCH_2), 3.09 (m, 6H, NCH_2), 1.99 (s, 9H, CH_3Ar) ppm. ^{13}C-NMR (101 MHz, CD_3CN): δ 167.65 (Ar*C*HN), 162.75 (Ar), 151.70 (Ar), 149.75 (Ar), 149.19 (Ar), 137.67 (Ar), 137.33 (Ar), 136.70 (Ar), 133.27 (Ar), 127.77 (Ar), 126.41 (Ar), 124.12 (Ar), 123.99 (Ar), 122.73 (Ar), 121.95 (Ar), 119.74 (Ar), 119.56 (Ar), 58.87 (N*C*H_2), 57.77 (N*C*H_2), 56.97 (N*C*H_2), 55.87 (N*C*H_2), 34.23 (*C*$(CH_3)_3$), 30.46 (C(*C*$H_3)_3$), 18.89 (Ar*C*H_3) ppm. Elemental analysis: Calculated for $C_{102}H_{114}Cu_3F_9N_{13}O_{12}S_6Y$: C 51.98, H 4.88, N 7.73. Found: C 51.86, H 4.86, N 7.86. ESI-MS: m/z: 2054.8 ($[LYCu_3(ArS)_3OTf]^+$)

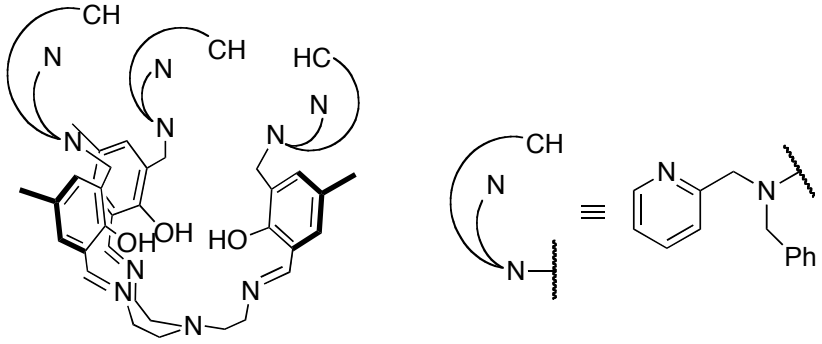
Synthesis of 12.



12

To a THF solution of 3-(chloromethyl)-2-hydroxy-5-methylbenzaldehyde (0.8969 g, 4.94 mmol) was added N-benzyl-N-(2-picolyl)amine (0.979 g, 4.94 mmol, 1 equiv). The solution turns from light brown to yellow. Triethylamine (2.4 mL, 17.28 mmol, 3.5 equiv) was added, and a yellow precipitate formed. The solution was allowed to stir at room temperature for 1 hour. The mixture was then filtered through Celite and the solvent removed *in vacuo* to obtain 1.465 g of crude product as a thick yellow oil (86%), which was carried on without further purification. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 10.33 (s, 1H, ArC*H*O), 8.59 (m, 1H, Ar*H*), 7.67 (m, 1H, Ar*H*), 7.41 (m, 9H, Ar*H*), 3.80 (s, 2H, NCH_2Ar), 3.76 (s, 2H, NCH_2Ar), 3.69 (s, 2H, NCH_2Ar), 3.48 (s, 1H, ArO*H*), 2.28 (s, 3H, CH_3Ar) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2): δ 191.90 (Ar*C*HO), 159.06 (Ar), 158.16 (Ar), 148.87 (Ar), 138.11 (Ar), 137.32 (Ar), 136.66 (Ar), 129.06 (Ar), 128.33 (Ar), 128.13 (Ar), 128.10 (Ar), 125.27 (Ar), 123.04 (Ar), 122.52 (Ar), 122.22 (Ar), 58.57 (N*C*H_2Ar), 57.84 (N*C*H_2Ar), 54.84 (N*C*H_2Ar), 55.45 (N*C*H_2Ar), 19.99 (Ar*C*H_3) ppm. HRMS (FAB), $C_{22}H_{23}N_2O_2$: calculated m/z = 3471760; observed m/z = 347.1775 ($M+H^+$).

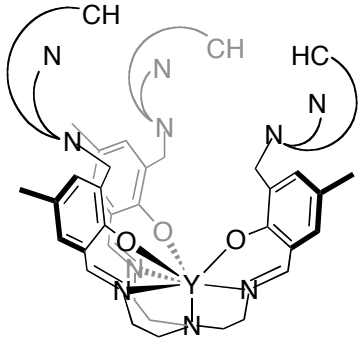
Synthesis of 13.



13

In a Schlenk tube, aldehyde **13** (1.465 g, 4.267 mmol, 3 equiv) was dried under vacuum for 1 hour. Tris(2-aminoethyl)amine (0.20 mL, 1.351 mmol, 1 equiv) was added via syringe under positive N_2 pressure. Dry methanol (15 mL) was transferred via cannula, and the mixture was stirred at room temperature for 12 hours. The solution was filtered through Celite and SiO_2, and the solvent removed *in vacuo* from the filtrate to obtain a yellow oil. The crude product was purified via SiO_2 column chromatography using 1% triethylamine in methanol as the eluent to obtain 0.640 g of product as a yellow solid (40%). ^{1}H-NMR (300 MHz, C_6D_6): δ 14.03 (s, 3H, ArO*H*), 8.38 (s, 6H, Ar*H*), 7.65 (s, 3H, NC*H*Ar), 7.51 (s, 3H, Ar*H*), 7.43 (m, 3H, Ar*H*), 7.13 (m, 12H, Ar*H*), 6.52 (m, 3H, Ar*H*), 5.72 (s, 3H, Ar*H*), 4.01 (s, 6H, NCH_2Ar), 4.00 (s, 6H, NCH_2Ar), 2.97 (br s, 6H, NCH_2CH$_2$N), 2.97 (br s, 6H, NCH$_2$CH_2N), 2.04 (s, 9H, CH_3Ar) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2): δ 166.19 (Ar*C*HN), 160.48 (Ar), 157.65 (Ar), 148.90 (Ar), 139.72 (Ar), 135.76 (Ar), 133.57 (Ar), 130.51 (Ar), 128.62 (2 superimposed peaks, Ar), 128.09 (2 superimposed peaks, Ar), 126.69 (Ar), 126.58 (Ar), 126.27 (Ar), 122.09 (Ar), 121.22 (Ar), 118.32 (Ar) 59.77 (N*C*H$_2$Ar), 58.45 (N*C*H$_2$Ar), 57.98 (NCH$_2$*C*H$_2$N), 55.45 (N*C*H$_2$CH$_2$N), 51.40 (N*C*H$_2$Ar), 20.24 (Ar*C*H$_3$) ppm. HRMS (FAB), $C_{72}H_{79}N_{10}O_3$: calculated m/z = 1131.634; observed m/z = 1131.6306 ($M+H^+$).

Synthesis of 14.

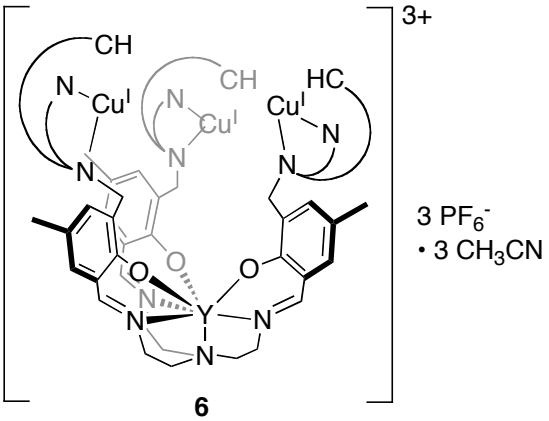


14

Yttrium complex **10** was prepared in a manner analogous to complex **3** (0.1505 g, 53%). %). ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 8.40 (m, 3H, Ar*H*), 8.03 (s, 3H, NC*H*Ar), 7.50 (m, 3H, Ar*H*), 7.37 (m, 3H, Ar*H*), 7.28 (m, 15H, Ar*H*), 7.04 (m, 3H, Ar*H*), 6.71 (br s, 3H, Ar*H*), 4.12 (m, 3H, NC*H*H'), 3.48 (m, 21H, NCH_2), 2.95 (m, 3H, NCH*H'*), 2.79 (m, 3H, NCH_2), 2.22 (s, 9H, CH_3Ar) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2): δ 167.93 (Ar*C*HN),

164.35 (Ar), 161.36 (Ar), 148.41 (Ar), 140.77 (Ar), 136.16 (Ar), 135.64 (Ar), 132.61 (Ar), 128.92 (Ar), 128.77 (Ar), 128.67 (Ar), 127.73 (Ar), 126.13 (Ar), 122.57 (Ar), 121.45 (Ar), 121.06 (Ar), 120.76 (Ar), 59.57 (N*C*H_2), 59.16 (N*C*H_2), 57.87 (N*C*H_2), 57.73 (N*C*H_2), 51.71 (N*C*H_2), 20.18 (Ar*C*H_3) ppm. Elemental analysis: Calc for $C_{72}H_{75}N_{10}O_3Y$: C 71.04, H 6.21, N 11.51. Found: C 70.87, H 6.11, N 11.54.

Synthesis of 6.



6

Yttrium-tricopper complex **6** was prepared in a manner analogous to complex **4** (0.164 g, 95%). ^{1}H-NMR (300 MHz, CD_3CN): δ 8.14 (m, 3H, Ar*H*), 8.04 (s, 3H, NC*H*Ar), 7.22 (m, 3H, Ar*H*), 7.20 (m, 21H, Ar*H*), 7.01 (m, 3H, Ar*H*), 6.56 (br s, 3H, Ar*H*), 4.15 (m, 3H, NC*H*H'), 3.62 (m, 3H, NCH_2), 3.48 (m, 18H, NCH_2), 3.15 (m, 3H, NCH*H'*), 2.96 (m, 3H, NCH_2), 2.10 (s, 9H, CH_3Ar) ppm. ^{13}C-NMR (101 MHz, CD_3CN): δ 168.06 (Ar*C*HN), 163.16 (Ar), 158.79 (Ar), 148.37 (Ar), 137.80 (Ar), 136.69 (Ar), 128.08 (Ar), 127.54 (Ar), 126.34 (Ar), 123.62 (Ar), 128.67 (Ar), 123.28 (Ar), 122.44 (Ar), 121.60 (Ar), 60.49 (N*C*H_2), 58.85 (N*C*H_2), 58.76 (N*C*H_2), 57.52 (N*C*H_2), 54.95 (N*C*H_2), 19.29 (Ar*C*H_3) ppm. Elemental analysis: Calculated for $C_{78}H_{84}Cu_3F_{18}N_{13}O_3P_3Y$: C 47.65, H 4.31, N 9.26. Found: C 47.78, H 4.38, N 9.19.

Synthesis of 7

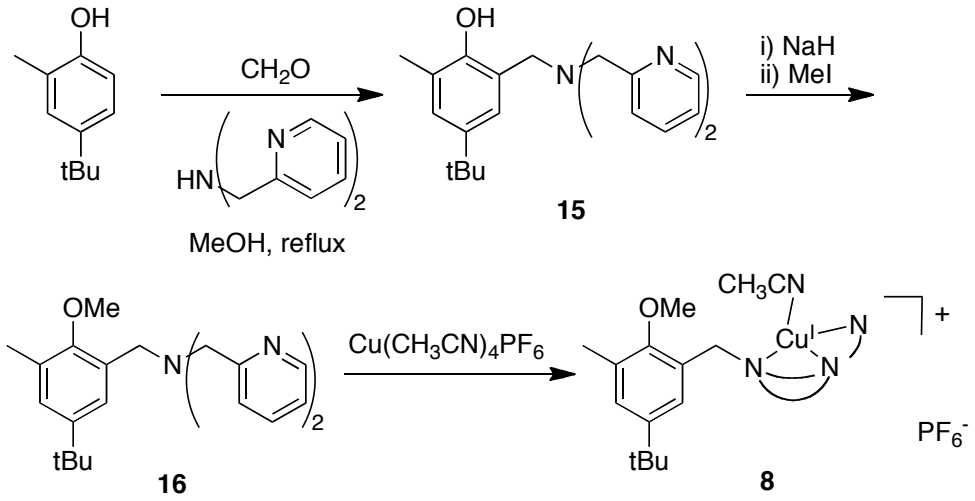
Compound **7** was prepared in a manner analogous to complex **5**. Identification by means of mass spectroscopy (ESI) was unsuccessful.

λ_{max}, nm (ε, $M^{-1}cm^{-1}$): 340 (11,500), 455 (2,160), 690 (760).

Reactions of 7 with substrates

Reactions of compound **7** with substrates were carried out in a manner analogous to reactions of complex **5**.

Reaction with triphenylphosphine was worked up by extraction of the dried reaction mixture with diethyl ether and the product was quantified by integration of its ^{31}P-NMR spectroscopy against excess triphenylphosphine starting material. The Cu-containing residue was dissolved in acetonitrile and was found to be a reduced tricopper(I) species (^{1}H-NMR, see below).



Scheme 1. Synthetic pathway for monoucleating ligand and monocopper complex

Synthesis of 15

4-tert-butyl-2-methylphenol (4.136 g, 25.18 mmol), formaldehyde (37% in water, 8.249 g, 0.1 mol, 4 equiv), and dipicolylamine (5.017 g, 25.18 mmol, 1 equiv) were dissolved in methanol and the mixture was refluxed overnight. The mixture was then cooled and a white precipitate formed. The solution was filtered to obtain the clean product as a colorless solid (6.134 g, 65 %). ^{1}H-NMR (300 MHz, C_6D_6): δ 11.00 (s, 1H, ArO*H*), 8.41 (m, 2H, Ar*H*), 7.19 (d, 1H, Ar*H*), 7.05 (m, 2H, Ar*H*), 6.94 (m, 3H, Ar*H*), 6.50 (m, 2H, Ar*H*), 3.79 (s, 4H, NCH_2Py), 3.62 (s, 2H, NCH_2Ar), 2.54 (s, 3H, ArCH_3), 1.29 (s, 6H, C(CH_3)$_3$) ppm. ^{13}C-NMR (101 MHz, C_6D_6): δ 158.64 (Ar), 154.04 (Ar), 148.84 (Ar), 140.39 (Ar), 135.78 (Ar), 127.27 (Ar), 124.43 (Ar), 124.37 (Ar), 122.85 (Ar), 121.54 (Ar), 121.35 (Ar), 58.99 (N*C*H$_2$Py), 57.56 (N*C*H$_2$Ar), 33.58 (Ar*C*(CH$_3$)$_3$), 31.54 (ArC(*C*H$_3$)$_3$), 16.59 (Ar*C*H$_3$) ppm. HRMS (FAB), $C_{24}H_{30}N_3O$: calculated m/z = 376.2389; observed m/z = 372.2381.

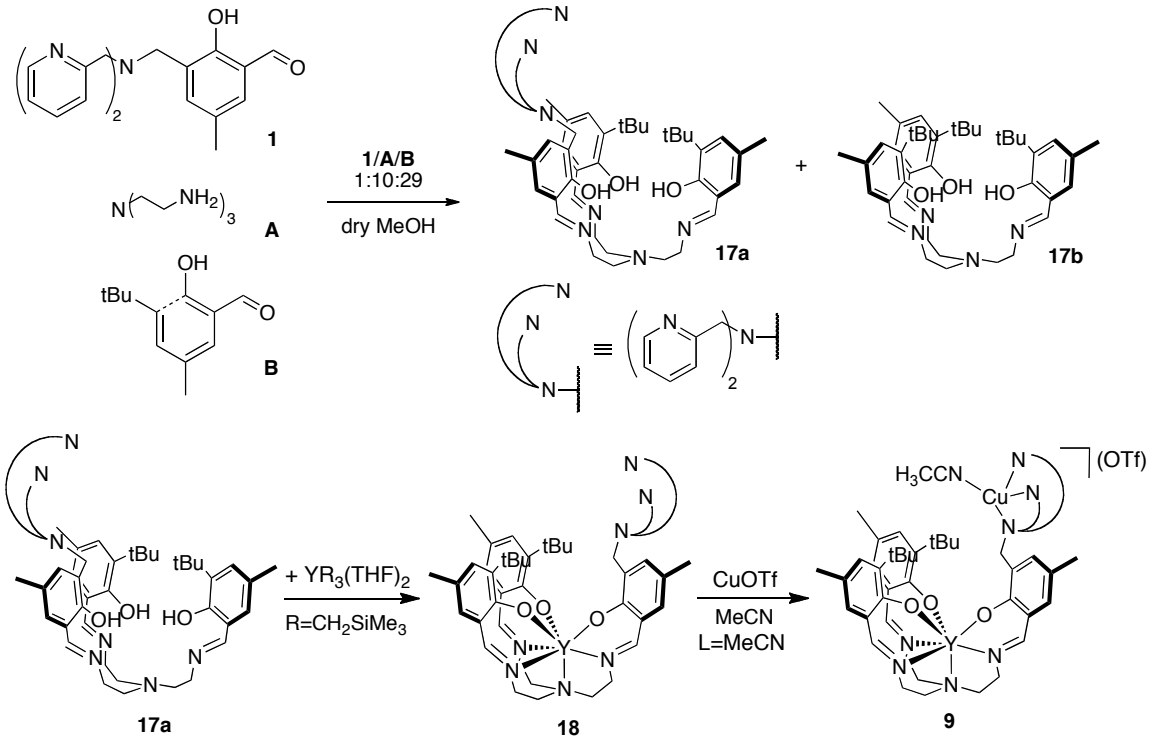
Synthesis of 16.

Compound **15** (2.0671 g, 5.50 mmol) was dried on a Schlenk line overnight in a Schlenk tube. THF was transferred to the reaction flask via cannula. NaH (0.1651 g, 6.88 mmol, 1.25 equiv) was added against positive N_2 pressure. The solution turned cloudy, and gas evolution was observed. After 1 hour, MeI (0.52 mL, 8.26 mmol, 1.5 eq) was added via syringe. The solution was stirred at 70 °C for four hours, after which it was cooled and extracted with DCM/H_2O. The organic layer was dried over $MgSO_4$, filtered, and evaporated to give the product as a dark red oil (1.801 g, 84%). ^{1}H-NMR (300 MHz, C_6D_6): δ 8.18 (m, 2H, Ar*H*), 7.51 (s, 1H, Ar*H*), 7.28 (m, 2H, Ar*H*), 6.86 (m, 3H, Ar*H*), 6.35 (m, 2H, Ar*H*), 3.74 (s, 4H, NCH_2Py), 3.63 (s, 2H, NCH_2Ar), 3.05 (s, 3H, ArOCH_3), 1.93 (s, 3H, ArCH_3), 1.04 (s, 6H, C(CH_3)$_3$) ppm. ^{13}C-NMR (101 MHz, C_6D_6): δ 160.29 (Ar), 155.35 (Ar), 148.98 (Ar), 145.96 (Ar), 135.43 (Ar), 131.28 (Ar), 129.86 (Ar), 126.72 (Ar), 125.29 (Ar), 122.48 (Ar), 121.35 (Ar), 60.15 (N*C*H$_2$Py), 59.68 (N*C*H$_2$Ar), 52.81 (ArO*C*H$_3$), 34.03 (Ar*C*(CH$_3$)$_3$), 31.36 (ArC(*C*H$_3$)$_3$), 16.11 (Ar*C*H$_3$) ppm. HRMS (FAB), $C_{25}H_{32}N_3O$: calculated m/z = 390.2545; observed m/z = 390.2529 ($M+H^+$).

Synthesis of 8.
Compound **16** was dried under vacuum at 70°C for four hours, after which it was brought into the glovebox. A MeCN solution of $Cu(CH_3CN)_4PF_6$ (0.1466 g, 0.393 mmol) was added dropwise to a stirring THF solution of **12** (0.1532 g, 0.393 mmol). The solution changed color from red to dark golden. The solvent was removed *in vacuo* to obtain the product in near-quantitative yield. ^{1}H-NMR (300 MHz, CD_6CN): δ 8.51 (m, 2H, Ar*H*), 7.76 (m, 2H, Ar*H*), 7.34 (m, 5H, Ar*H*), 7.11 (br s, 1H, Ar*H*), 3.99 (br s, 2H, NCH_2Ar), 3.84 (s, 2H, NCH_2Py), 3.06 (s, 3H, ArOCH_3), 2.23 (s, 3H, ArCH_3), 1.23 (s, 6H, C(CH_3)$_3$) ppm. ^{13}C-NMR (101 MHz, CD_3CN): δ 153.12 (Ar), 155.45 (Ar), 148.74 (Ar), 146.29 (Ar), 137.69 (Ar), 130.43 (Ar), 128.79 (Ar), 127.27 (Ar), 127.05 (Ar), 123.79 (two overlapping peaks, Ar), 60.12 (N*C*H$_2$Py), 58.88 (N*C*H$_2$Ar), 54.88 (ArO*C*H$_3$), 33.77 (Ar*C*(CH$_3$)$_3$), 30.63 (ArC(*C*H$_3$)$_3$), 15.60 (Ar*C*H$_3$) ppm. Elemental analysis: Calculated for $C_{27}H_{34}CuF_6N_4OP$: C 50.74, H 5.36, N 8.77. Found: C 51.02, H 5.29, N 8.62.

Reaction of 8 with O_2.
Compound **8** was reacted with O_2 in a manner analogous to complexes **4** and **6**.
λ_{max}, nm (ε, $M^{-1}cm^{-1}$): 675 (100).

Preparation of 9
Yttrium-monocopper complex **9** required synthesis of the asymmetric ligand **17a** (Scheme 2) via an imine condensation route analogous to the preparation of **2**. Reaction of **1** with a large excess (10 equiv) of tren followed by addition of 29 equivalents of 3-*tert*-butylsalicylaldehyde gave a mixture of the desired ligand (**17a**) and the symmetric trialkyl ligand **17b**, most of which precipitates from the reaction solution. Unfortunately, upon concentration *in vacuo* often led, in the presence of adventitious water, to scrambling of the ligand arms to give a mixture of asymmetric and symmetric ligands. A mixture (consisting mostly of **19**, which was the only dipicolylamine-containing species) was therefore used for metalation with yttrium analogous to preparation of **3**. Yttrium complex **19** was obtained as part of a complex mixture due to the impurities in the ligand material. Thus, **19** was reacted with a substoichiometric amount of Cu^I salt to afford the yttrium-monocopper complex **9**.



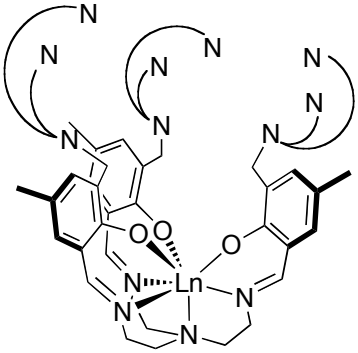
Scheme 2. Synthethic pathway to **9**

*Synthesis of **9**.*

In a 500 mL Schlenk flask, 1.55 mL tren (10.3 mmol, 10 equiv) was dissolved in dry methanol. **1** (0.3950 g, 1.03 mmol) was dissolved in DCM and added to the tren solution dropwise. After 15 minutes, 3-*tert*-butyl-2-hydroxybenzaldehyde (5.7619 g, 29.97 mmol, 29 equiv) [ref] was added as a DCM solution. Over 20 minutes, a yellow precipitate formed. The reaction was stirred for 2 hours, after which activated 3Å molecular sieves were added to the solution. After 20 minutes, the reaction solution was opened to air and rapidly filtered through Celite to remove most of the unwanted side product and molecular sieves. The filtrate was concentrated *in vacuo*, redissolved in DCM, and passed through a short silica gel plug. DCM (1 L) was eluted to remove as much of the symmetric trialkyl ligand (**17b**) as possible, after which ligand **17a** was eluted with methanol. Solvent was removed from the methanol fraction and the resulting yellow powder (~0.500 g) was brought into the glovebox. ^{1}H-NMR revealed a 5:1 mixture of **17a** to **17b**. **17a**: ^{1}H-NMR (300 MHz, C_6D_6): δ 8.40 (m, 2H, *o*-Py*H*), 7.77 (m, 6H, Ar*H*+ArC*H*N), 7.14 (m, 2H, Ar*H*), 7.07 (m, 3, Ar*H*), 6.54 (m, 2H, Py*H*), 5.66 (s, 3H, Ar*H*), 4.13 (m, 6H, NCH_2), 2.97 (s, 6H, NCH_2), 2.13 (m, 15H, NCH_2), 1.60 (s, 18H, ArC(CH_3)). ^{13}C-NMR (101 MHz, CD_2Cl_{20}): δ 166.66 (Ar*C*HN), 166.18 (Ar*C*HN), 159.83 (Ar), 157.93 (Ar), 157.91 (Ar), 148.78 (Ar), 136.40 (Ar), 136.05 (Ar), 130.53 (Ar), 130.19 (Ar), 129.73 (Ar), 129.61 (Ar), 126.25 (Ar), 126.19 (Ar), 122.44(Ar), 121.66(Ar), 118.38(Ar), 118.29(Ar), 67.69 (N*C*H$_2$), 60.05 (N*C*H$_2$), 58.14 (N*C*H$_2$), 56.11 (N*C*H$_2$), 51.75 (N*C*H$_2$), 34.50 (N*C*H$_2$), 29.10 (C(*C*H$_3$)$_3$), 25.52 (*C*(CH$_3$)$_3$), 20.11, 20.01 (Ar*C*H$_3$) ppm. ESI-MS: 824.1 (M^+)

Part of the ligand-containing mixture (0.1968 g, 0.239 mmol) was dissolved in THF and the solution frozen. Upon thawing, a thawing solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.1123 g, 0.227 mmol, 0.95 equiv) in THF was added dropwise. The solution was warmed to room temperature and stirred for 3 hours. The solvent was removed *in vacuo* and the resulting yellow solid was washed with hexanes, diethyl ether, toluene, and THF. The diethyl ether and toluene fractions were combined and evaporated to dryness to give a material consisting mostly of yttrium complex **18**. This complex was suspended in acetonitrile, and $Cu(CH_3CN)_4OTf$ (0.100 mmol) was added as acetonitrile solution. The solution changed from colorless to yellow as **18** was complexed. The solution was filtered through celite to remove unreacted **18** and the solvent was evaporated to give **9** as a golden yellow powder. ^{1}H-NMR (400 MHz, CD_3CN) δ 8.22 (m, 2H, Py*H*), 8.01 (s, 1H, ArC*H*N), 7.97 (m, 2H, ArC*H*N), 7.95 (s, 3H, ArC*H*N), 7.50 (m, 2H, Py*H*), 7.07 (m, 2H, Py*H*), 6.91 (d, 1.8 Hz, 1H, Ar*H*), 6.80 (d, 1.8 Hz, 1H, Ar*H*), 6.76 (d, 1.8 Hz, 1H, Ar*H*), 6.74 (m, 2H, Py*H*), 6.66 (d, 1.8 Hz, 1H, Ar*H*), 6.63 (d, 1.8 Hz, 1H, Ar*H*), 6.42 (d, 1.8 Hz, 1H, Ar*H*), 4.04-3.75 (m, 5H, CH_2), 3.22-2.65 (m, 13H, NCH_2), 1.97 (s, 3H, CH_3Ar), 1.85 (s, 3H, CH_3Ar), 1.84 (s, 3H, CH_3Ar), 1.01 (s, 9H, $C(CH)_3$), 0.77 (s, 9H, $C(CH)_3$) ppm. ^{13}C-NMR (101 MHz, CD_3CN): δ 168.39 (Ar*C*HN), 167.97 (Ar*C*HN), 167.55 (Ar*C*HN), 164.51 (Ar), 148.47 (Ar), 139.68 (Ar), 139.32 (Ar), 137.69 (Ar), 137.53 (Ar), 134.44 (Ar), 132.03 (Ar), 131.91 (Ar), 131.69 (Ar), 125.168 (Ar), 123.46 (Ar), 121.74 (Ar), 121.61 (Ar), 121.07 (Ar), 120.94 (Ar), 60.17 (NCH_2), 59.61 (NCH_2), 58.37 (NCH_2), 58.07 (NCH_2), 57.88 (NCH_2), 54.25 (NCH_2), 34.49 ($C(CH_3)_3$), 34.19 ($C(CH_3)_3$), 29.30 ($C(CH_3)_3$), 28.65 ($C(CH_3)_3$), 19.74 (ArCH_3), 19.64 (ArCH_3), 19.14 (ArCH_3) ppm. ESI-MS: 972.4 ([M - OTf - CH_3CN]$^+$).

General procedure for metallation of 2 with lanthanide metals (La, Lu)



Ln = La (**19**), Lu (**20**)

The procedure for the synthesis of all lanthanide complexes of **2** was analogous to that for preparation of **3**. The procedure to prepare lanthanum complex **20** is given as an example.

Synthesis of 19

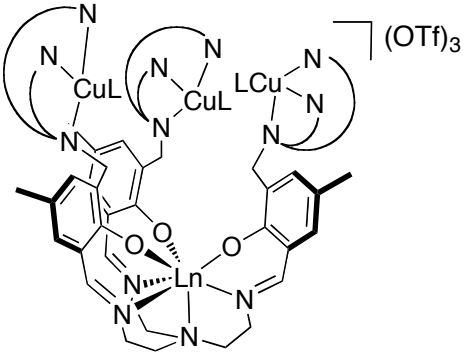
In a glovebox, 0.1917 g **2** (169 μmol) was dissolved in THF and the solution frozen. Separately, $La[N(SiMe_3)_2]_3$ (0.1048 g, 169 μmol, 1 equiv) was dissolved in THF and this solution also frozen. Upon thawing, the La solution was added to the stirring ligand solution dropwise. The solution was allowed to warm to room temperature. After 2

hours, volatiles were removed *in vacuo*. The resulting solid was washed with hexanes, diethyl ether, toluene, and THF. The THF fraction was collected and volatiles removed *in vacuo* to give the desired product as a yellow powder (0.0978 g, 46%). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.41 (s, 6H, *o*-Py*H*), 8.02 (s, 3H, ArC*H*NCH$_2$), 7.48 (m, 6H, Py*H*), 7.36 (m, 6H, Py*H*), 7.10 (d, 2.4 Hz, 3H, Ar*H*), 7.02 (m, 6H, Py*H*), 6.70 (d, 2.4 Hz, 3H, Ar*H*), 3.67 (m, 6H, NCH_2CH_2N), 3.54 (s, 12H, NCH_2Ar), 3.43 (s, 6H, NCH$_2$Ar), 2.80 (m, 6H, NCH_2CH_2N), 2.36 (s, 3H, NC*H*H'Ar), 2.18 (s, 9H, CH_3Ar) 1.29 (m, 3H, NCH*H'*Ar). ^{13}C-NMR (101 MHz, CD_2Cl_2): δ 167.28 (Ar*C*HN), 163.88 (Ar), 160.75 (Ar), 148.49 (Ar), 135.79 (Ar), 135.67 (Ar), 133.02 (Ar), 128.01 (Ar), 122.77 (Ar), 121.51 (Ar), 121.27 (Ar), 121.17 (Ar), 61.30 (N*C*H$_2$), 59.63 (N*C*H$_2$), 59.17 (N*C*H$_2$), 52.70 (N*C*H$_2$), 20.03 (Ar*C*H$_3$) ppm. HRMS (FAB), $C_{69}H_{73}LaN_{13}O_3$: calculated m/z = 1270.502; observed m/z = 1270.500 (M+H$^+$)

Synthesis of 20

Isolated as a yellow powder (46%). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.37 (s, 6H, *o*-Py*H*), 8.01 (s, 3H, ArC*H*NCH$_2$), 7.49 (m, 6H, Py*H*), 7.33 (m, 6H, Py*H*), 7.14 (d, 2.4 Hz, 3H, Ar*H*), 7.02 (m, 6H, Py*H*), 6.64 (d, 2.4 Hz, 3H, Ar*H*), 4.19 (m, 3H, NCH_2), 3.39 (m, 18H, NCH_2), 3.05 (m, 9H, NCH_2), 2.18 (s, 9H, CH_3Ar). ^{13}C-NMR (101 MHz, CD_2Cl_2): δ 167.91 (Ar*C*HN), 164.94 (Ar), 161.15 (Ar), 148.45 (Ar), 136.32 (Ar), 135.59 (Ar), 132.40 (Ar), 128.78 (Ar), 122.65 (Ar), 121.33 (Ar), 121.04 (Ar), 59.41 (N*C*H$_2$), 57.65 (2 superimposed signals, N*C*H$_2$), 52.18 (N*C*H$_2$), 20.13 (Ar*C*H$_3$) ppm. HRMS (FAB), $C_{69}H_{73}LuN_{13}O_3$: calculated m/z = 1306.537; observed m/z = 1306.535 (M+H$^+$)

General procedure for preparation of lanthanide-tricopper complexes



Ln = La (**10**), Lu (**11**)
L=MeCN

The procedure for the synthesis of all lanthanide-tricopper complexes was analogous. The procedure to prepare **10** is given as an example.

Synthesis of 10

In a glovebox, **19** (0.0978g, 77.0 μmol) was suspended in MeCN, and a MeCN solution of Cu(CH$_3$CN)$_4$OTf (0.0870 g, 231 μmol, 3 equiv) was added. The solution turned clear and golden yellow immediately. Volatiles were removed *in vacuo* to give the desired product in quantitative yield as a golden yellow powder. ^{1}H-NMR (400 MHz, CD_3CN): δ 8.45 (s, 6H, *o*-Py*H*), 8.14 (s, 3H, ArC*H*NCH$_2$), 7.60 (m, 6H, Py*H*), 7.28 (m, 6H, Py*H*), 6.97 (d, 2.4 Hz, 3H, Ar*H*), 6.82 (d, 2.4 Hz, 3H, Ar*H*), 6.78 (m, 6H, Py*H*), 4.25-3.25 (m,

21H, NCH_2), 3.11 (m, 9H, NCH_2), 2.05 (s, 9H, CH_3Ar). ^{13}C-NMR (101 MHz, CD_3CN): δ 167.99 (Ar*C*HN), 164.06 (Ar), 157.54 (Ar), 148.48 (Ar), 138.25 (Ar), 137.50 (Ar), 135.40 (Ar), 125.03 (Ar), 123.55 (Ar), 123.32 (Ar), 122.01 (Ar), 121.01 (Ar), 60.69 (N*C*H_2), 60.18 (N*C*H_2), 59.45 (N*C*H_2), 55.25 (N*C*H_2), 19.14 (Ar*C*H_3) ppm. Elemental analysis: Calculated for $C_{78}H_{81}Cu_3F_9LaN_{16}O_{12}S_3$: C 46.12, H 4.02, N 11.03. Found: C 46.02, H 3.90, N 10.84.

Synthesis of 11.

Isolated as a golden yellow powder (quantitative). ^{1}H-NMR (300 MHz, CD_3CN): δ 8.47 (s, 6H, *o*-Py*H*), 8.25 (s, 3H, ArC*H*NCH_2), 7.77 (m, 6H, Py*H*), 7.34 (m, 6H, Py*H*), 7.16 (d, 2.4 Hz, 3H, Ar*H*), 7.03 (m, 6H, Py*H*), 6.85 (d, 2.4 Hz, 3H, Ar*H*), 4.30 (m, 3H, ArC*H*H'N), 3.86 (m, 3H, NCH*H'*Ar), 3.58-2.76 (m, 24H, NCH_2), 2.10 (s, 9H, CH_3Ar). ^{13}C-NMR (101 MHz, CD_3CN): δ 167.65 (Ar*C*HN), 164.67 (Ar), 157.46 (Ar), 148.64 (Ar), 138.28 (Ar), 137.61 (Ar), 134.31 (Ar), 125.79 (Ar), 123.75 (Ar), 123.35 (Ar), 122.03 (Ar), 121.59 (Ar), 58.64 (N*C*H_2), 57.48 (two superimposed peaks, N*C*H_2), 54.21 (N*C*H_2), 19.36 (Ar*C*H_3) ppm. Elemental analysis: Calculated for $C_{78}H_{81}Cu_3F_9LuN_{16}O_{12}S_3$: C 45.32, H 3.95, N 10.84. Found: C 45.22, H 3.77, N 10.76.

Nuclear Magnetic Resonance Spectra

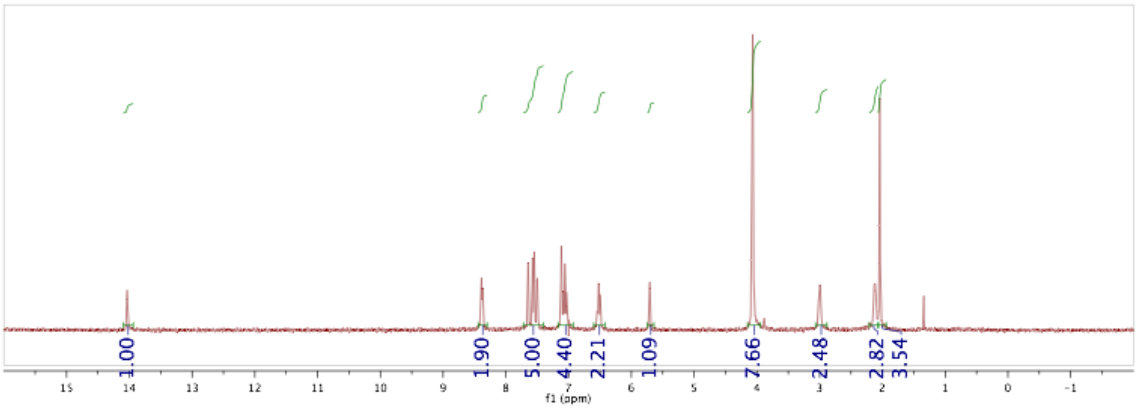


Figure S1. ^{1}H-NMR spectrum of **2** in C_6D_6.

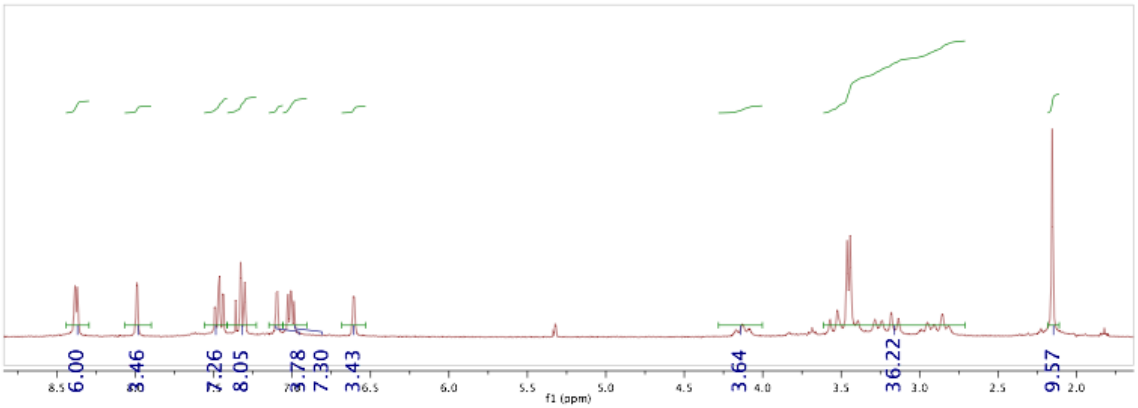


Figure S2. ^{1}H-NMR spectrum of **3** in CD_2Cl_2.

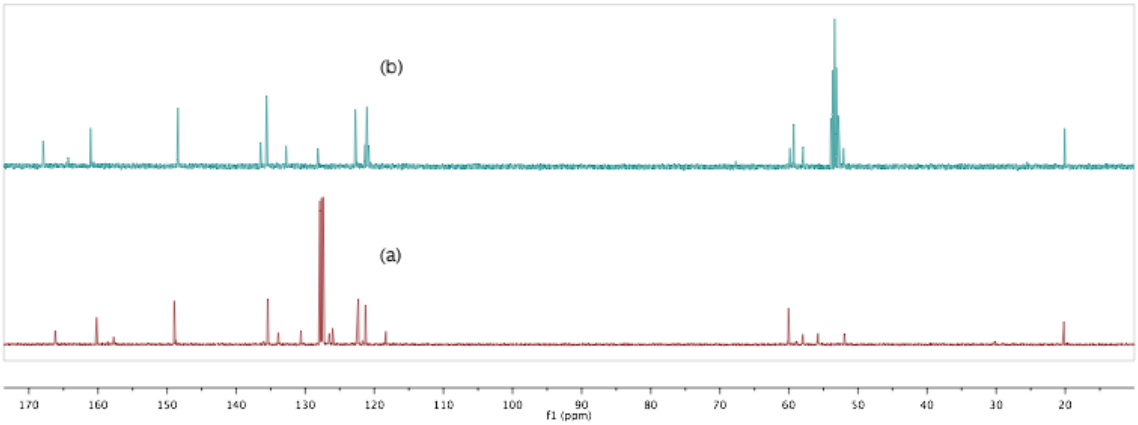


Figure S3. ^{13}C-NMR spectra of (a) **2** (in C_6D_6) and (b) **3** (in CD_2Cl_2).

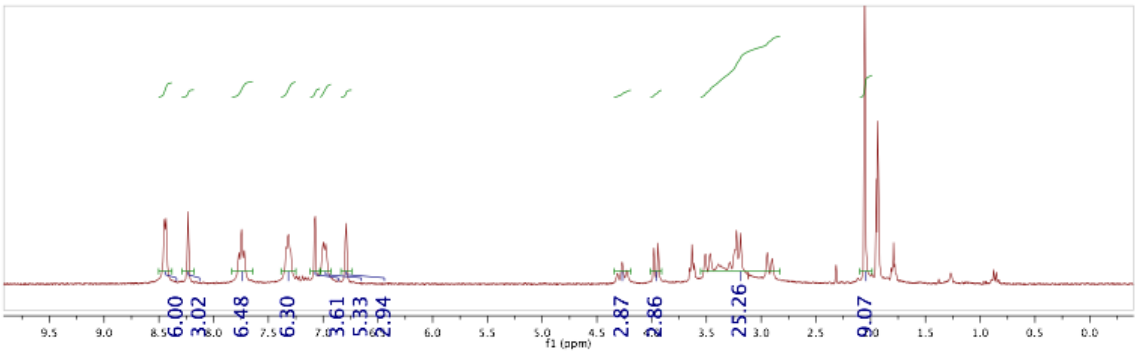


Figure S4. ^{1}H-NMR spectrum of **4** in CD_3CN**.**

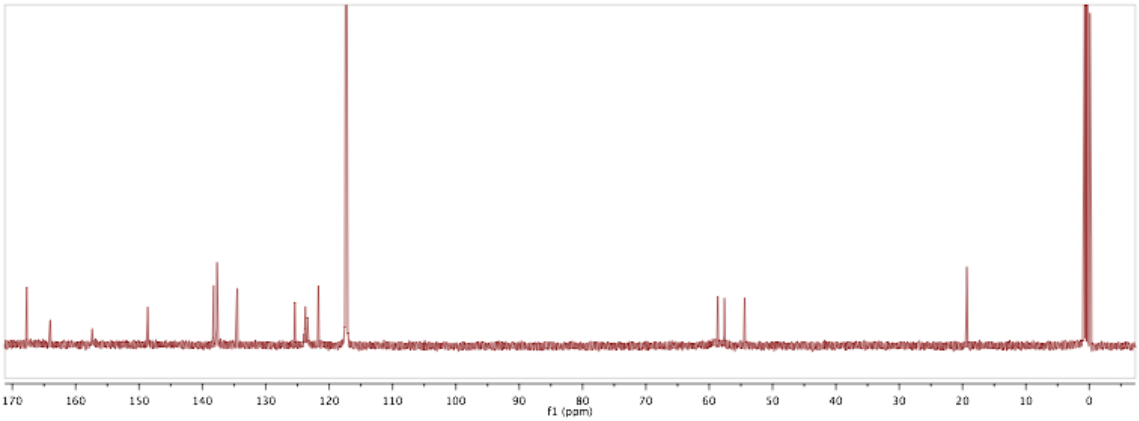


Figure S5. ^{13}C-NMR spectrum of **4** in CD_3CN.

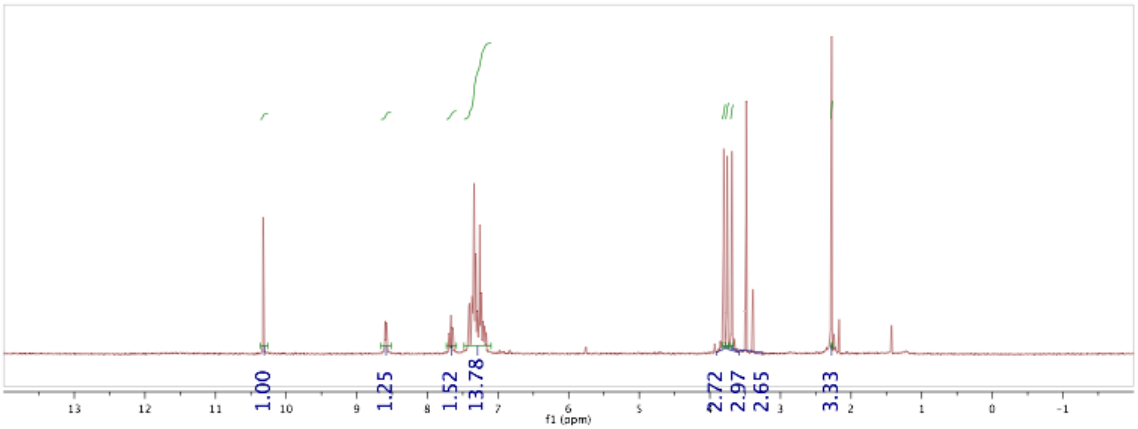


Figure S6. ^{1}H-NMR spectrum of **12** in CD_2Cl_2.

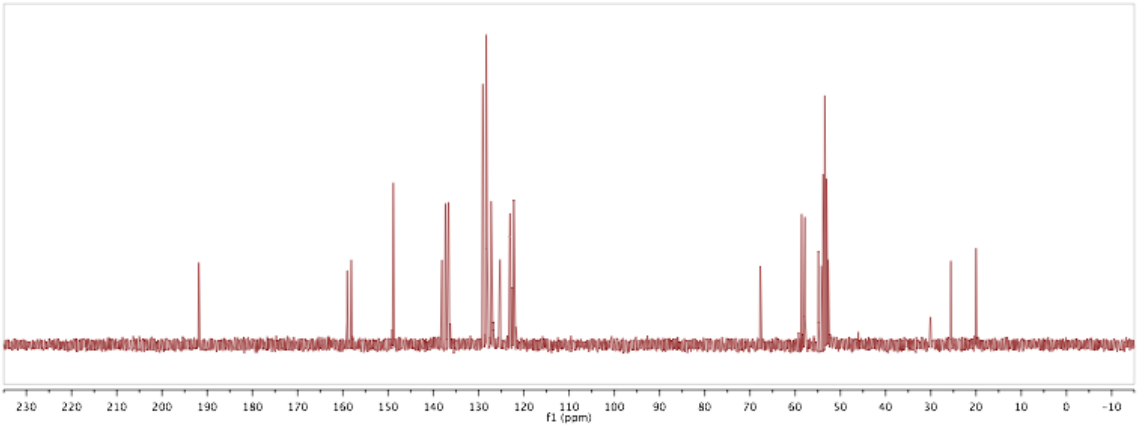


Figure S7. ^{13}C-NMR spectrum of **12** in CD_2Cl_2.

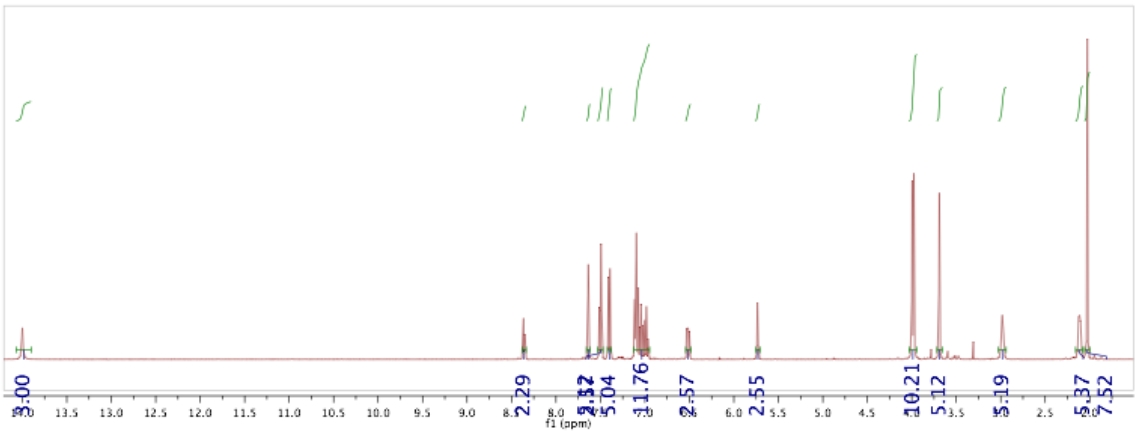


Figure S8. ^{1}H-NMR spectrum of **13** in C_6D_6.

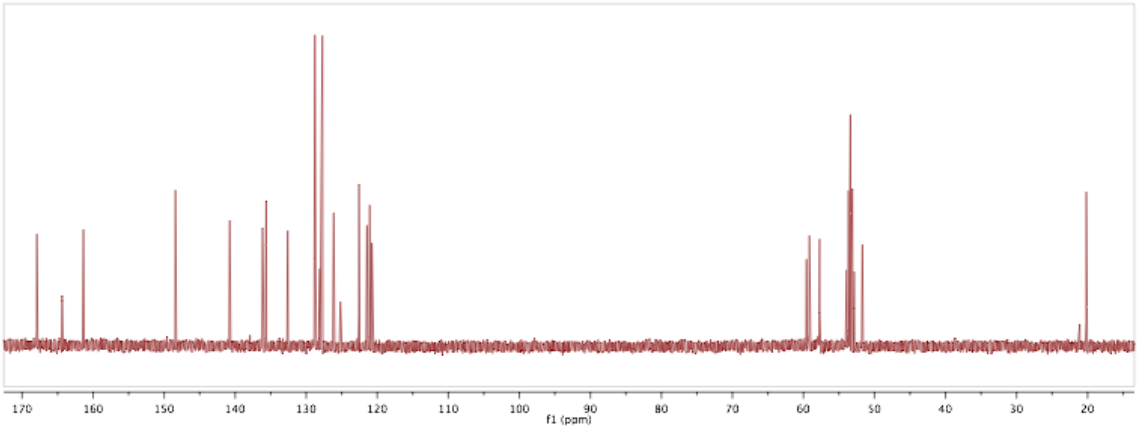


Figure S9. ^{13}C-NMR spectrum of **13** in C_6D_6.

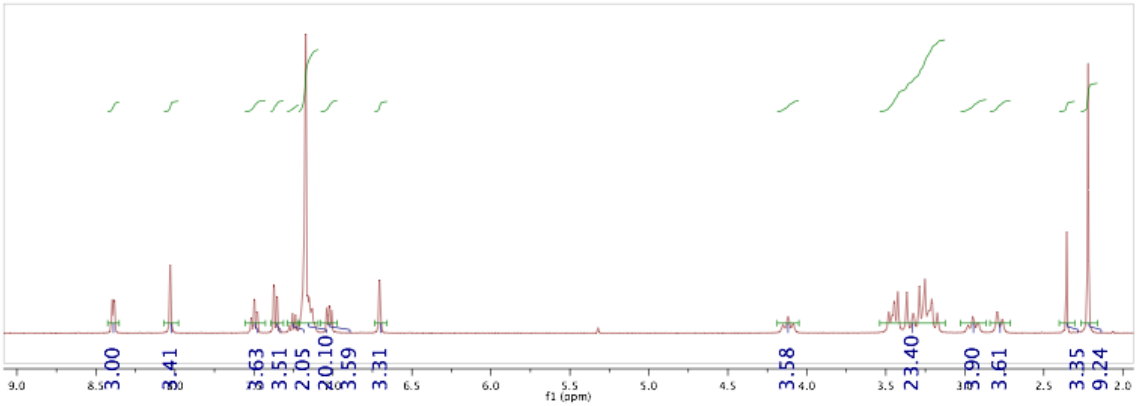


Figure S10. ^{1}H-NMR spectrum of **6** (in CD_3CN).

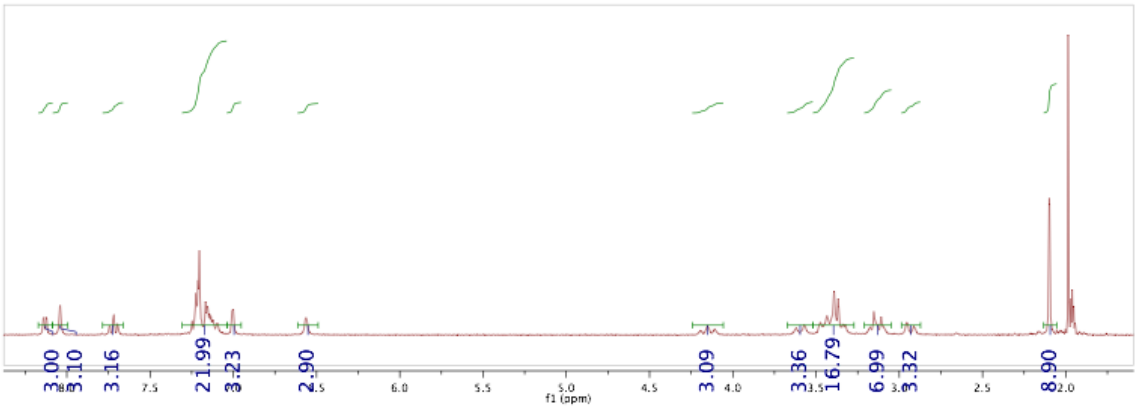


Figure S11. ^{1}H-NMR spectrum of **14** in CD_3CN.

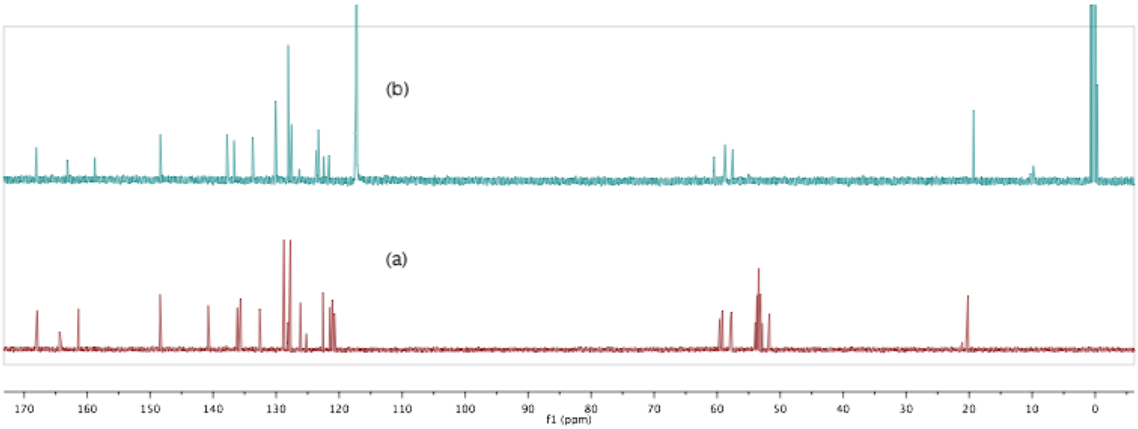


Figure S12. ^{13}C-NMR spectra of (a) **14** (in CD_2Cl_2) and (b) **6** (in CD_3CN).

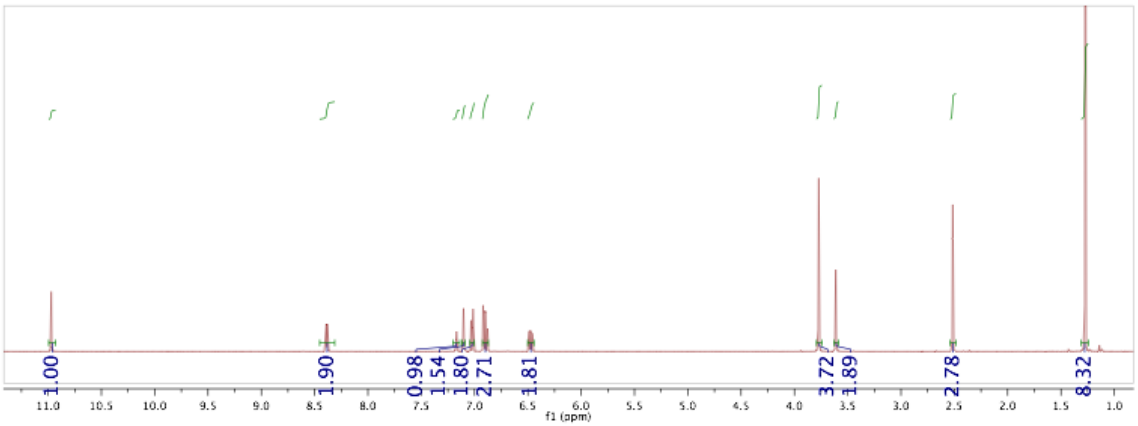


Figure S13. ^{1}H-NMR spectrum of **15** in C_6D_6.

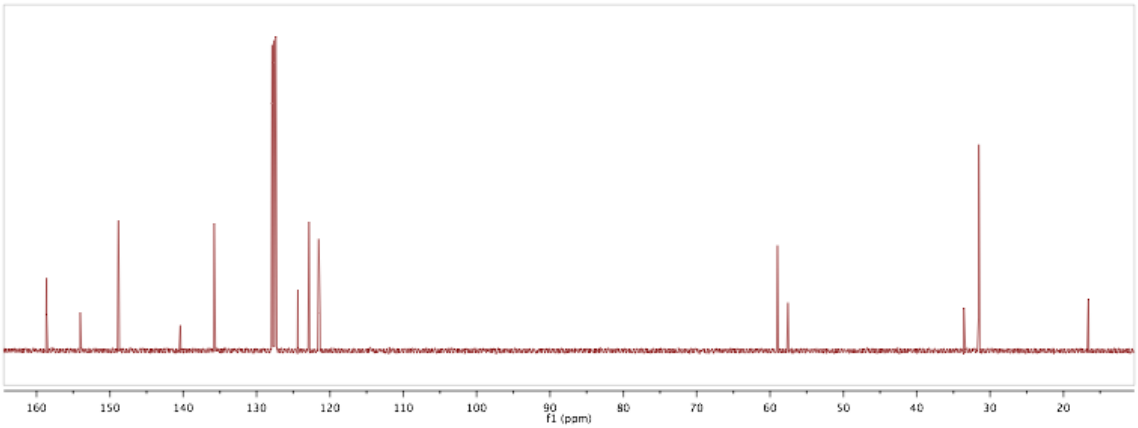


Figure S14. ^{13}C-NMR spectrum of **15** in C_6D_6.

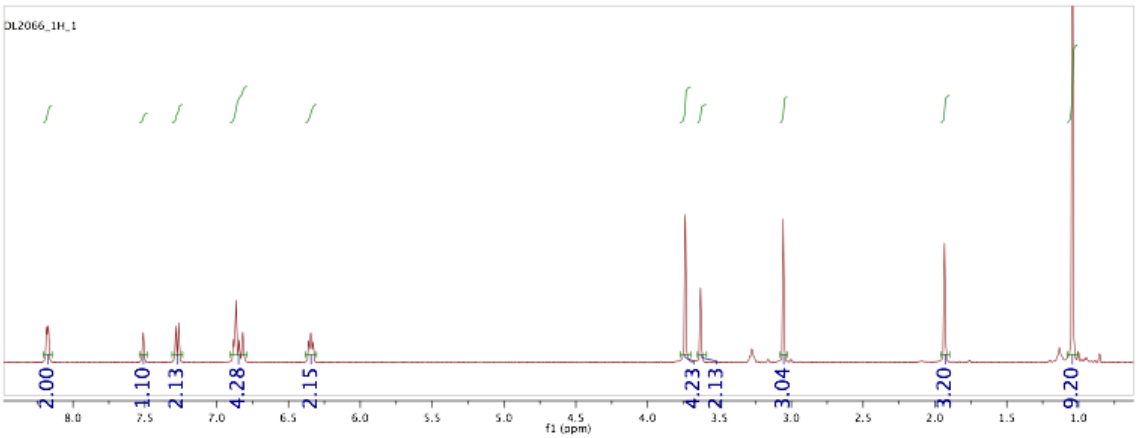


Figure S15. ^{1}H-NMR spectrum of **16** in C_6D_6.

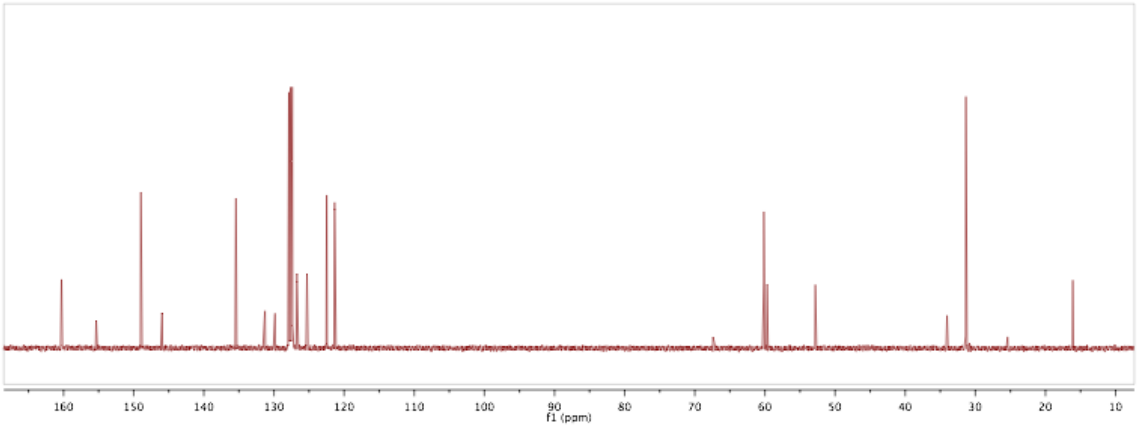


Figure S16. ^{13}C-NMR spectrum of **16** in C_6D_6.

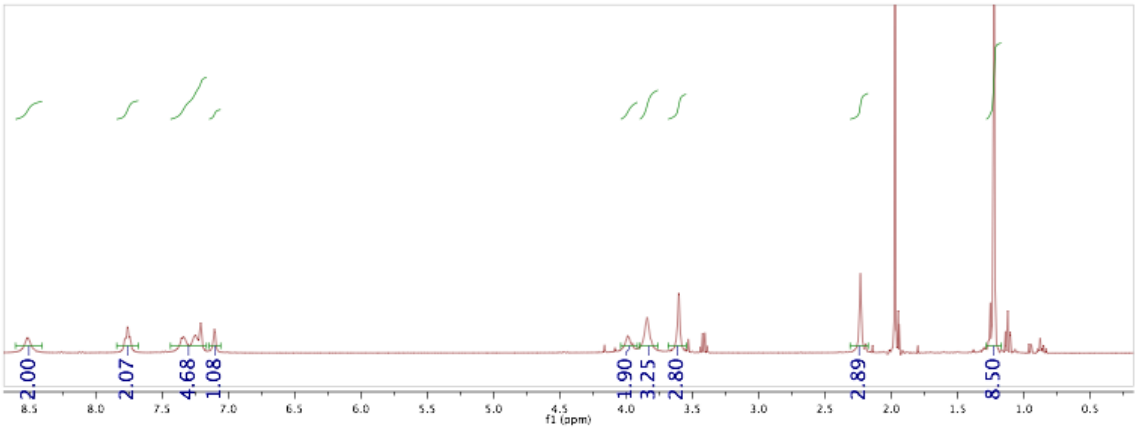


Figure S17. ^{1}H-NMR spectrum of **8** in CD_3CN.

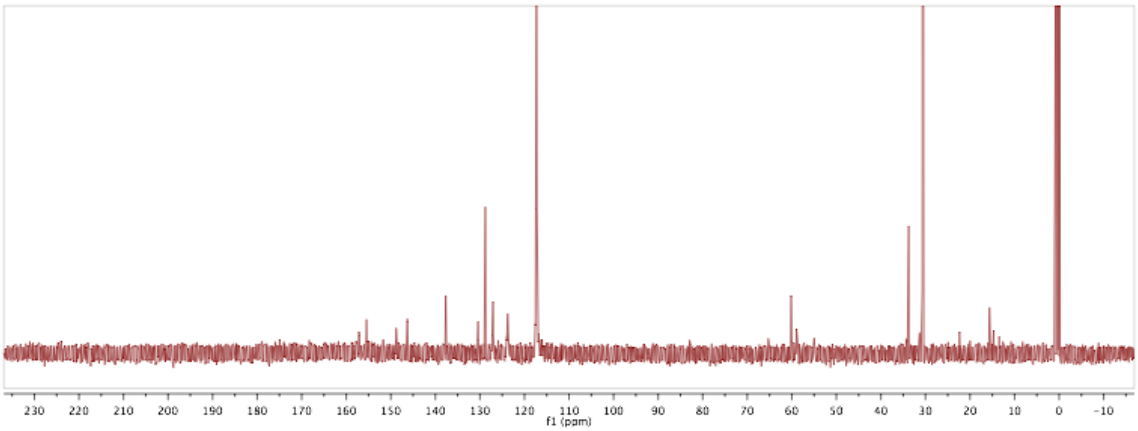


Figure S18. ^{13}C-NMR spectrum of **8** in CD_3CN.

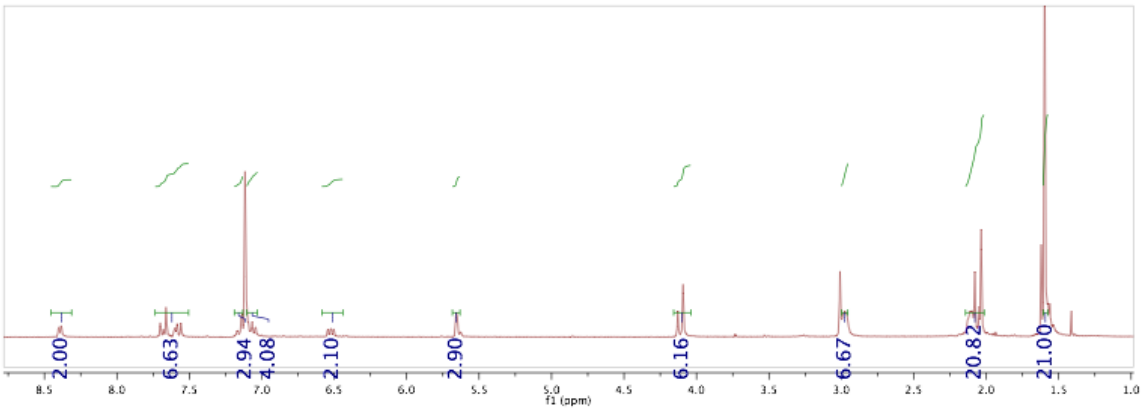


Figure S19. ^{1}H-NMR spectrum of **17a** in C_6D_6.

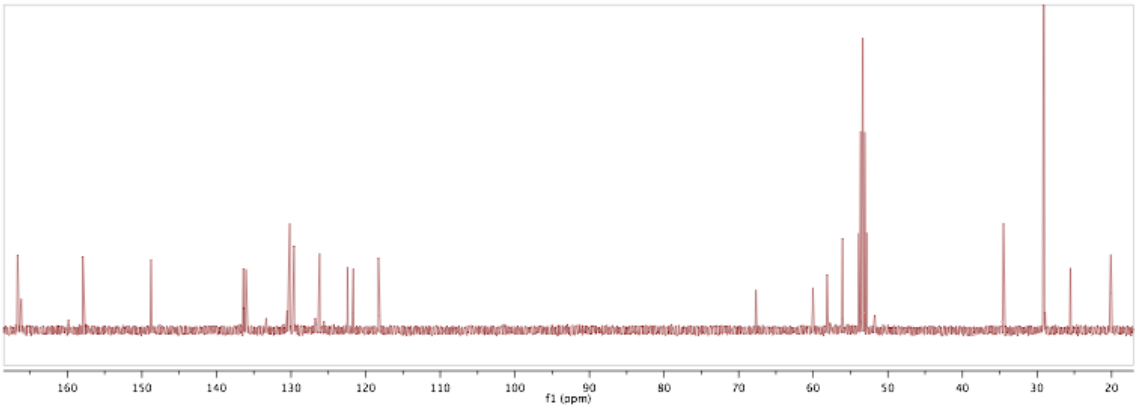


Figure S20. ^{13}C-NMR spectrum of **17a** in CD_2Cl_2.

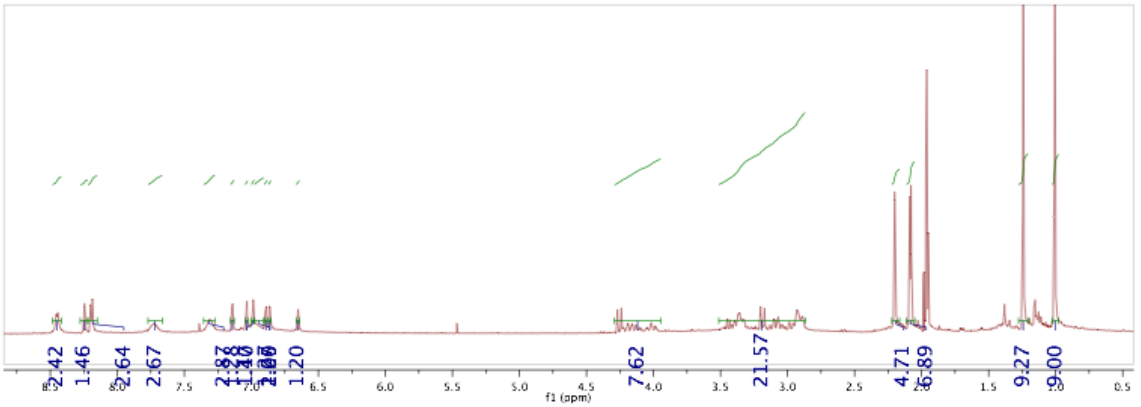


Figure S21. ^{1}H-NMR spectrum of **9** in CD_3CN.

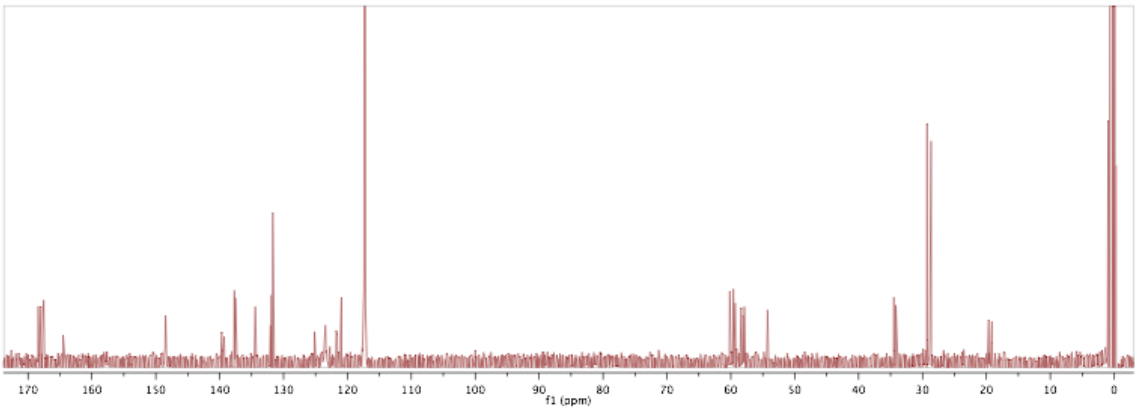


Figure S22. ^{13}C-NMR spectrum of **9** in CD_3CN.

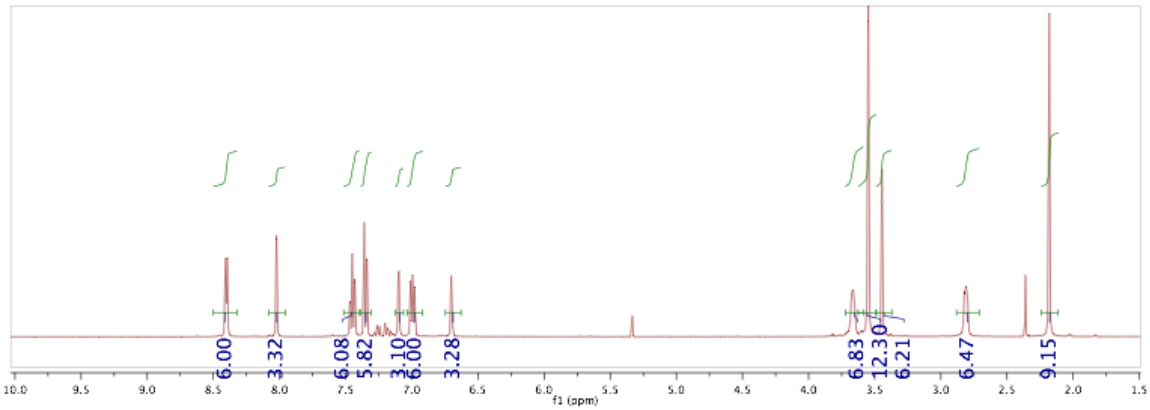


Figure S23. ^{1}H-NMR spectrum of **19** in CD_2Cl_2.

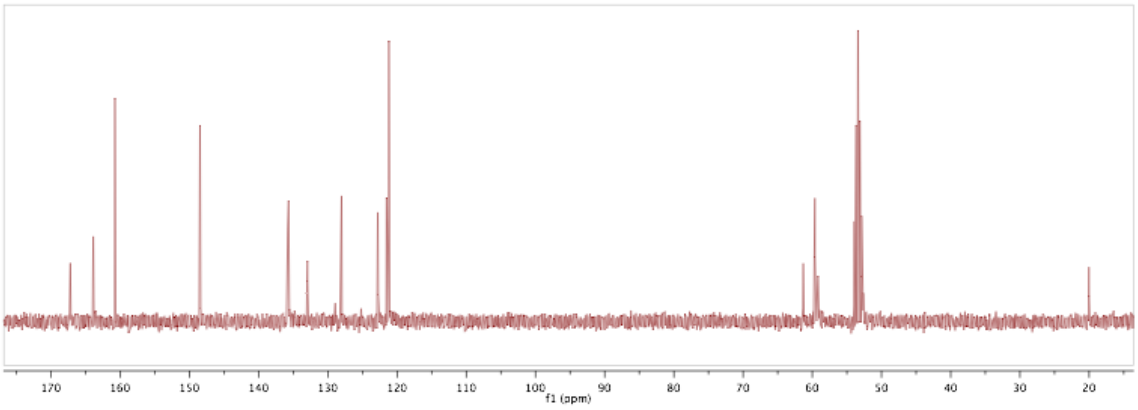


Figure S24. ^{13}C-NMR spectrum of **19** in CD_2Cl_2.

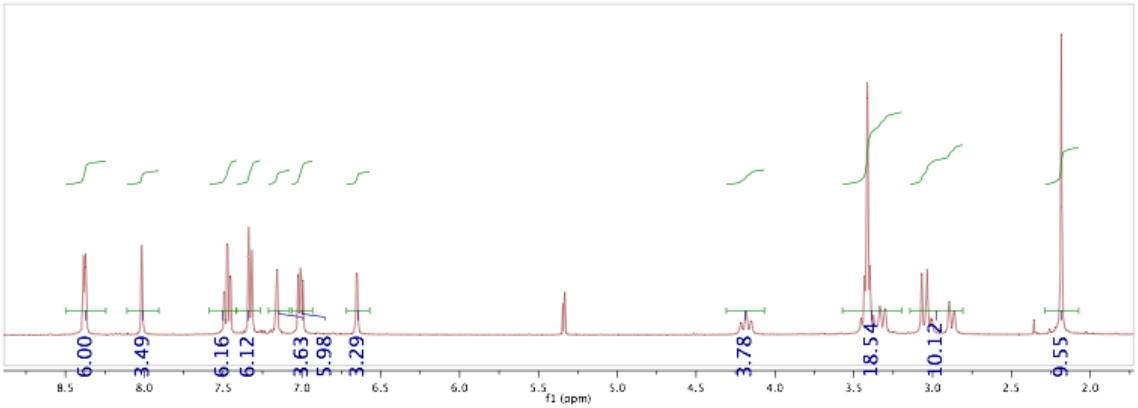


Figure S25. ^{1}H-NMR spectrum of **20** in CD_2Cl_2.

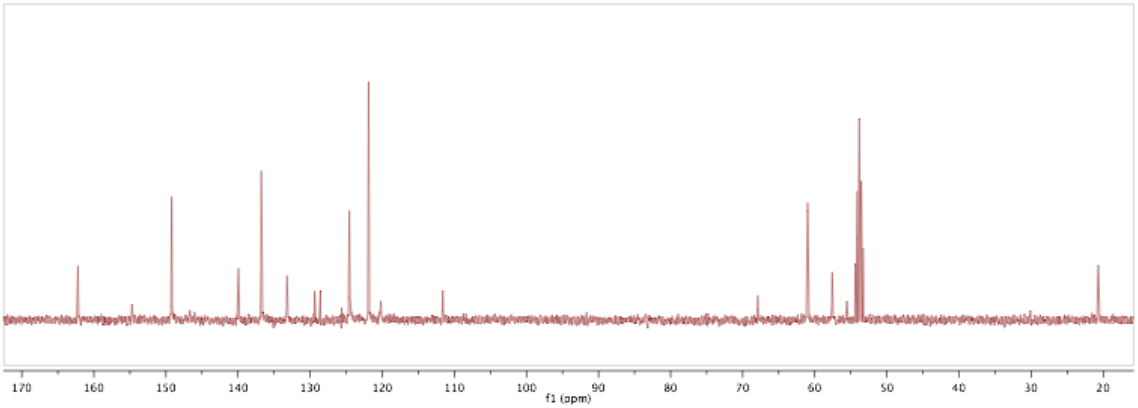


Figure S26. ^{13}C-NMR spectrum of **20** in CD_2Cl_2.

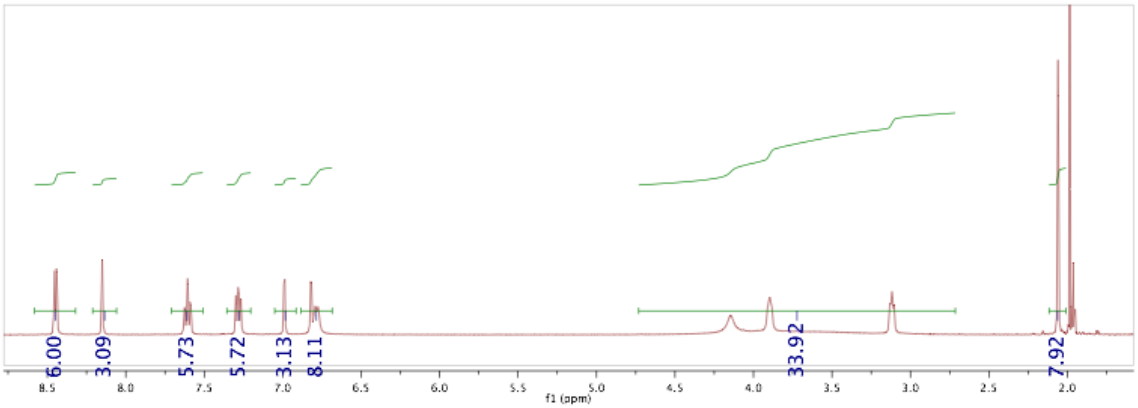


Figure S27. ^{1}H-NMR spectrum of **10** in CD_3CN.

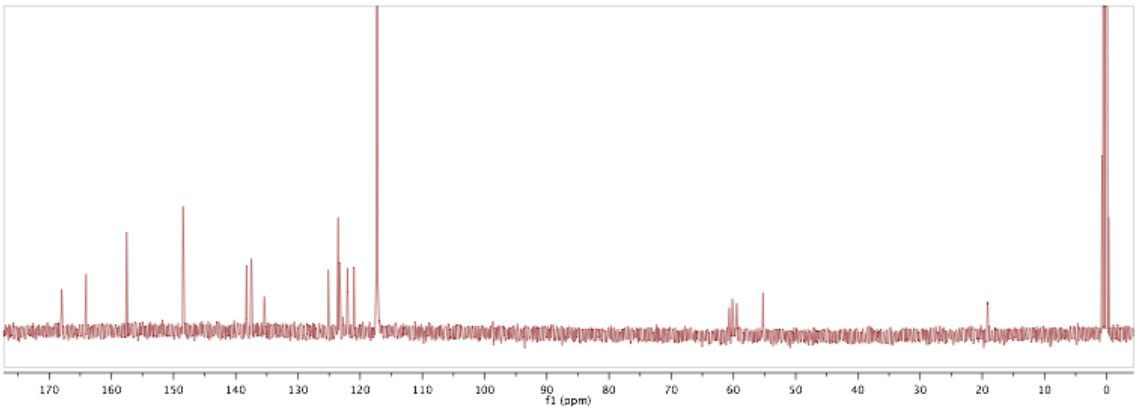


Figure S28. ^{13}C-NMR spectrum of **10** in CD_3CN.

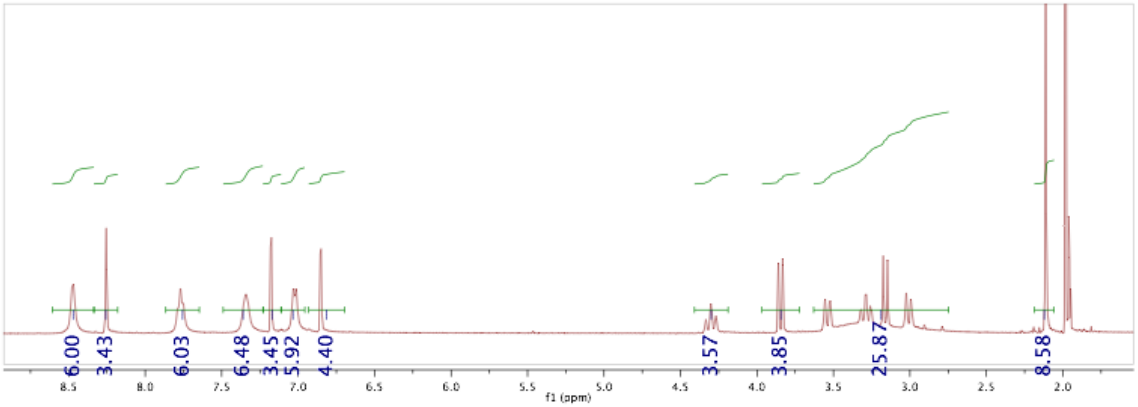


Figure S29. ^{1}H-NMR spectrum of **11** in CD_3CN.

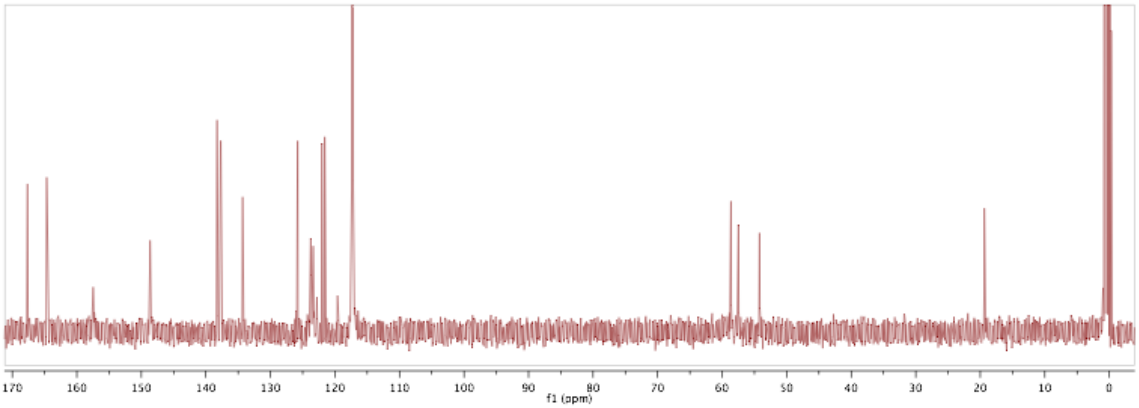


Figure S30. ^{13}C-NMR spectrum of 11 in CD_3CN.

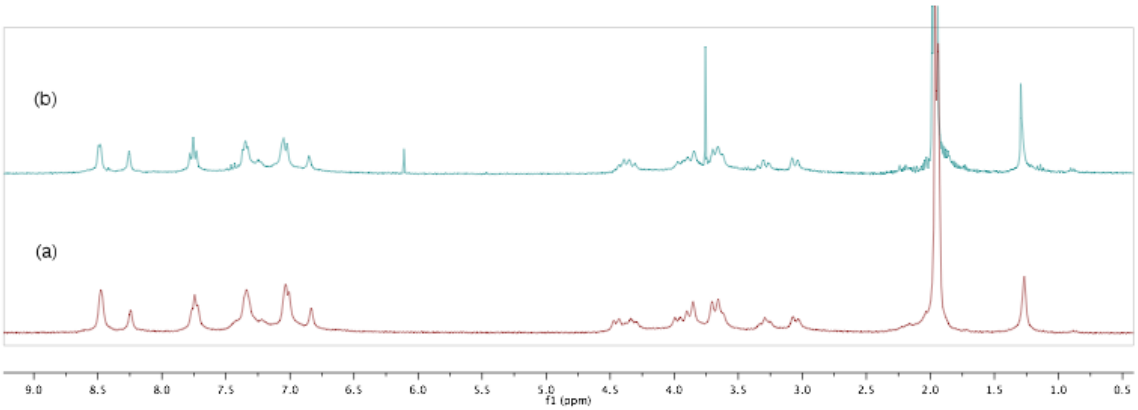


Figure S31. ^{1}H-NMR spectrum in CD_3CN of (a) **4**•$(ArSH)_3$ from reaction of **4** with 4-*tert*-butylthiophenol; (b) **4**•$(ArSH)_3$ from reaction of **5** with 4-*tert*-butylthiophenol

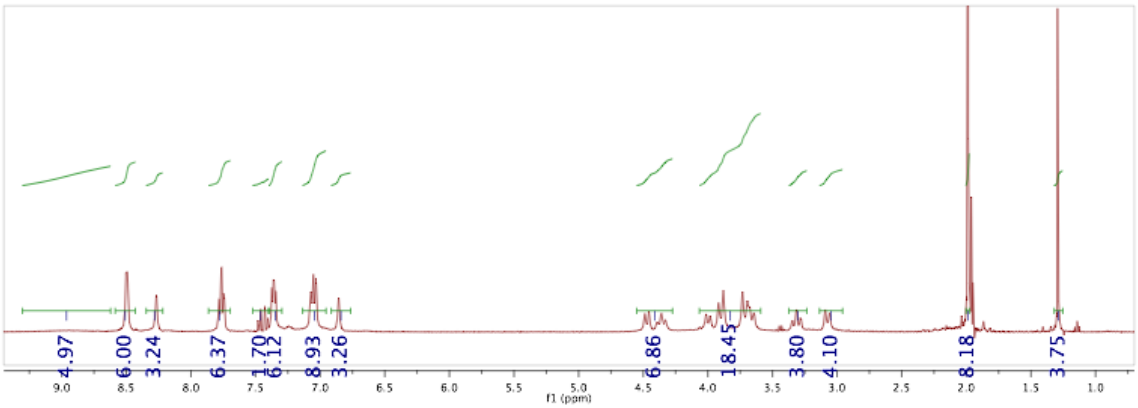


Figure S32. ^{1}H-NMR spectrum in CD_3CN of **4**•$(ArSH)_3$ from reaction of **4** with 4-*tert*-butylthiophenol

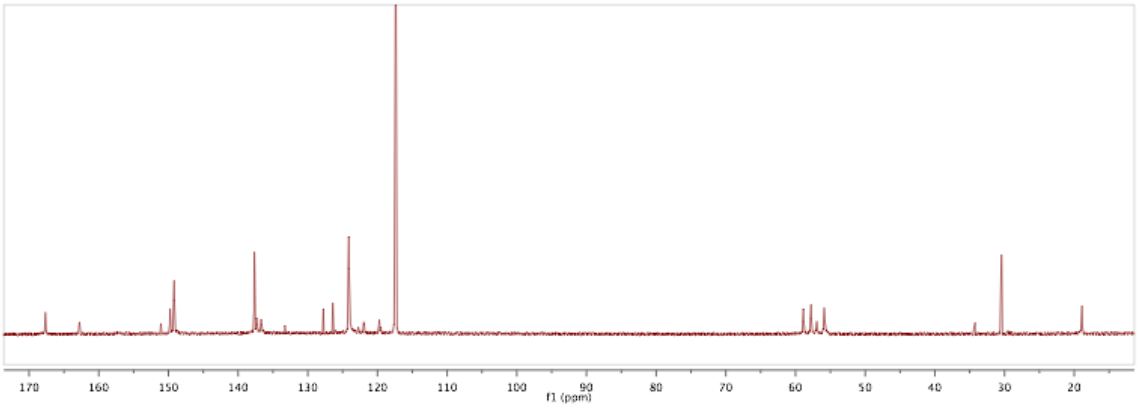


Figure S33. ^{13}C-NMR spectrum in CD_3CN of **4**•$(ArSH)_3$ from reaction of **4** with 4-*tert*-butylthiophenol.

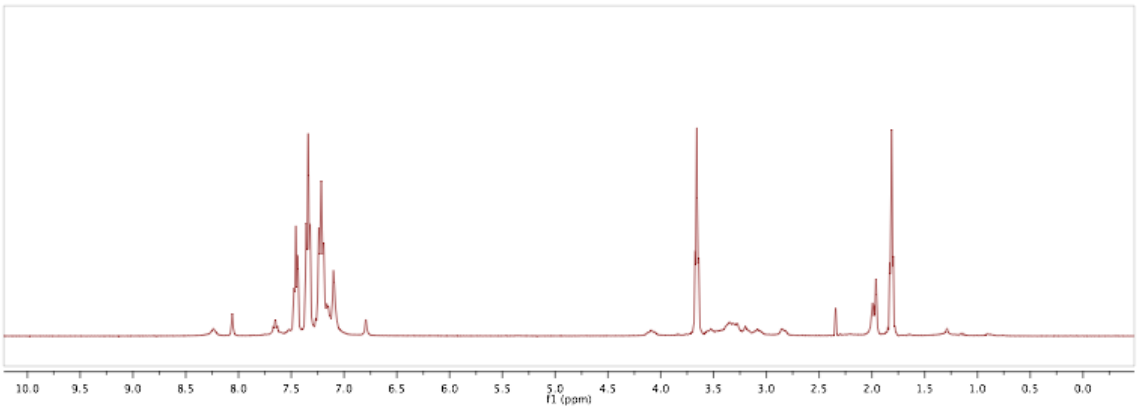


Figure S34. ^{1}H-NMR spectrum in CD_3CN of the Cu(I)-containing material from reaction of **7** with PPh_3.

UV-Vis spectra

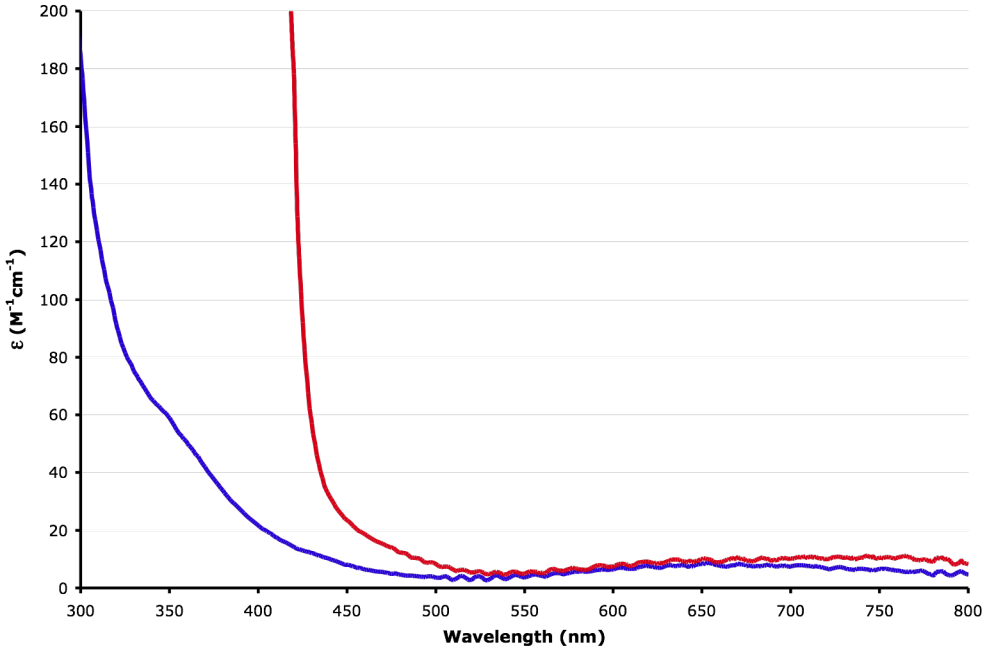


Figure S35. UV-Vis spectra of solutions of **8** (blue) and **9** (red) after addition of dioxygen in 1:1 propionitrile/ tetrahydrofuran at -78 °C.

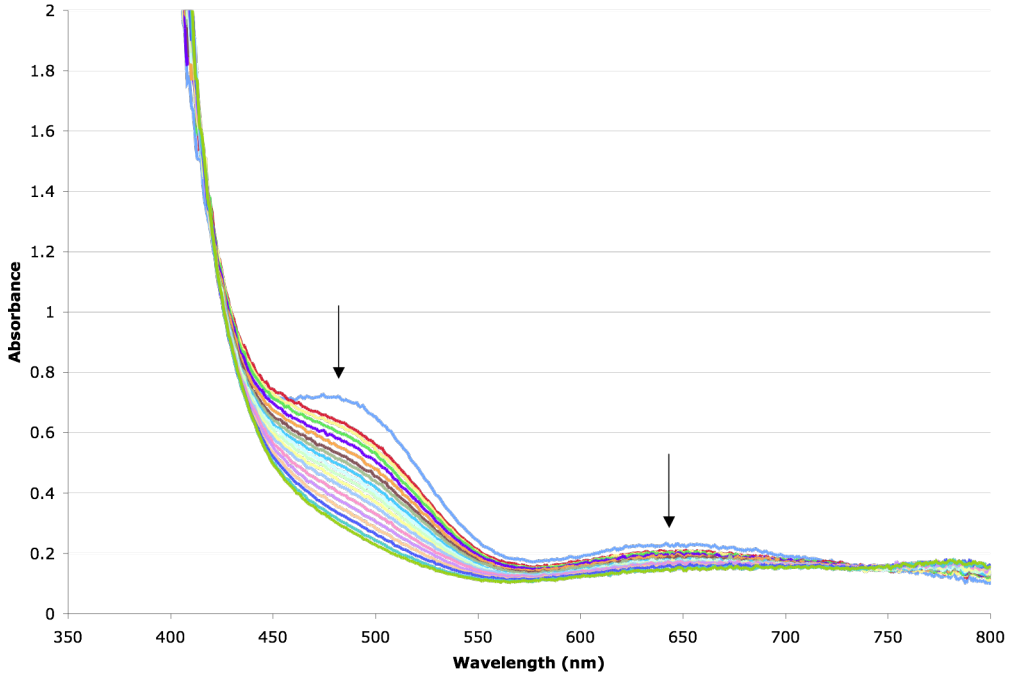


Figure S36. UV-Vis spectra of reaction of **5** (0.304 mM) with decamethylferrocene (4 eq) in 1:1 toluene/MeCN at -40 °C. Scan interval: 20 min. Total reaction time: 6 hours.

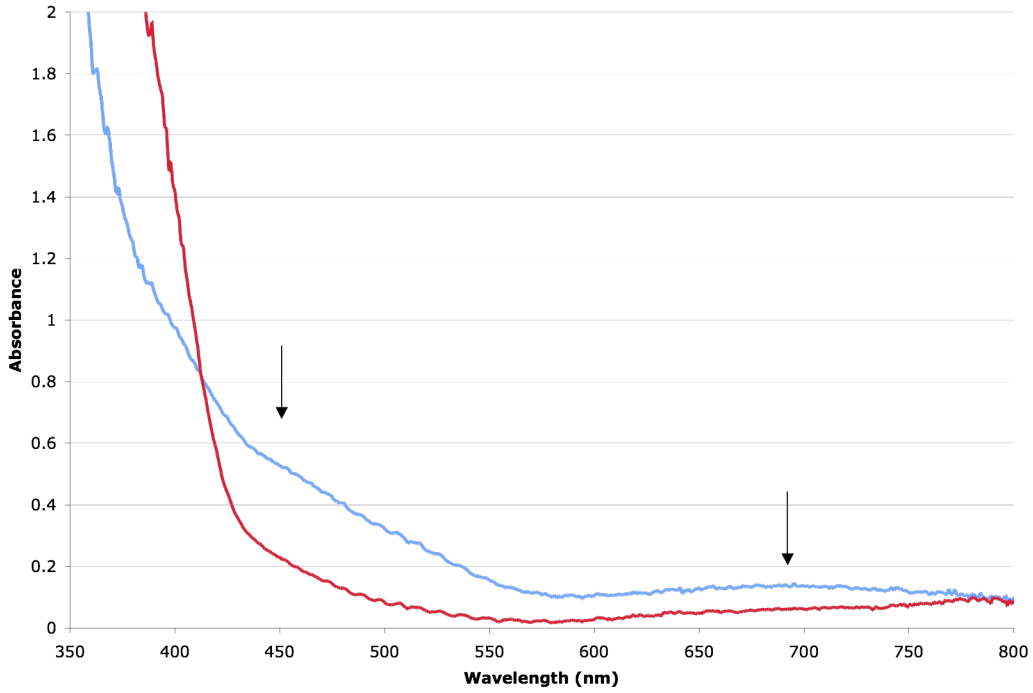


Figure S37. UV-Vis spectrum of **7** (0.182 mM, blue) at -40 °C; and after reaction with decamethylferrocene (5 eq) at -40 °C (red) over 6 hours.

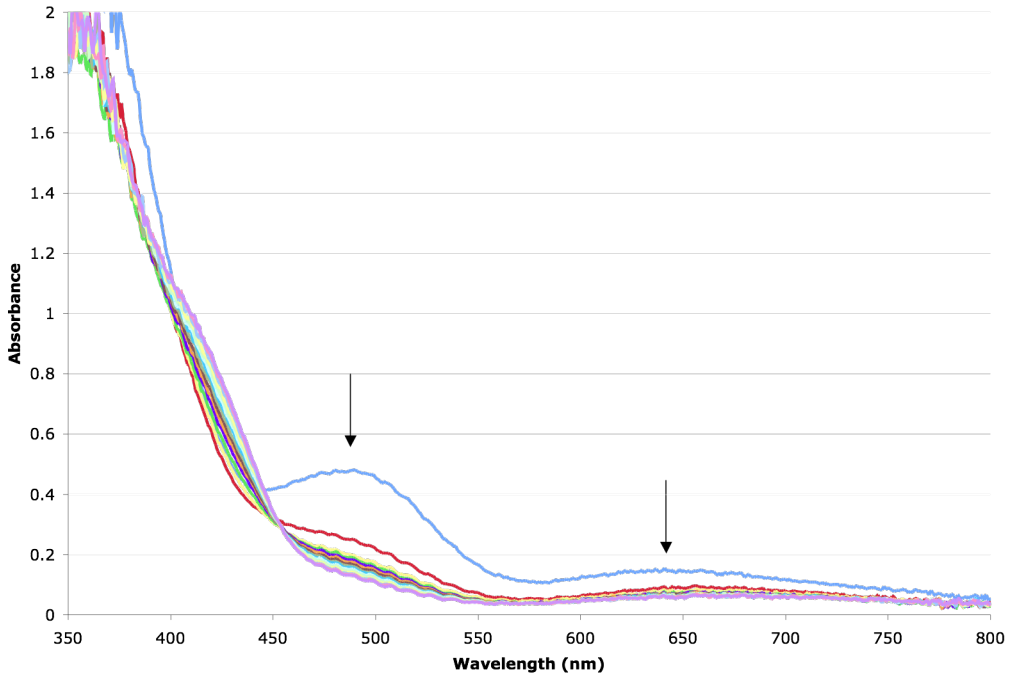


Figure S38. UV-Vis spectrum of reaction of **5** (0.169 mM) with $Et_3NH^+OTf^-$ (10 eq) in 3:2 toluene/acetonitrile at -40 °C. Scan interval: 20 minutes. Total reaction time: 4 hours.

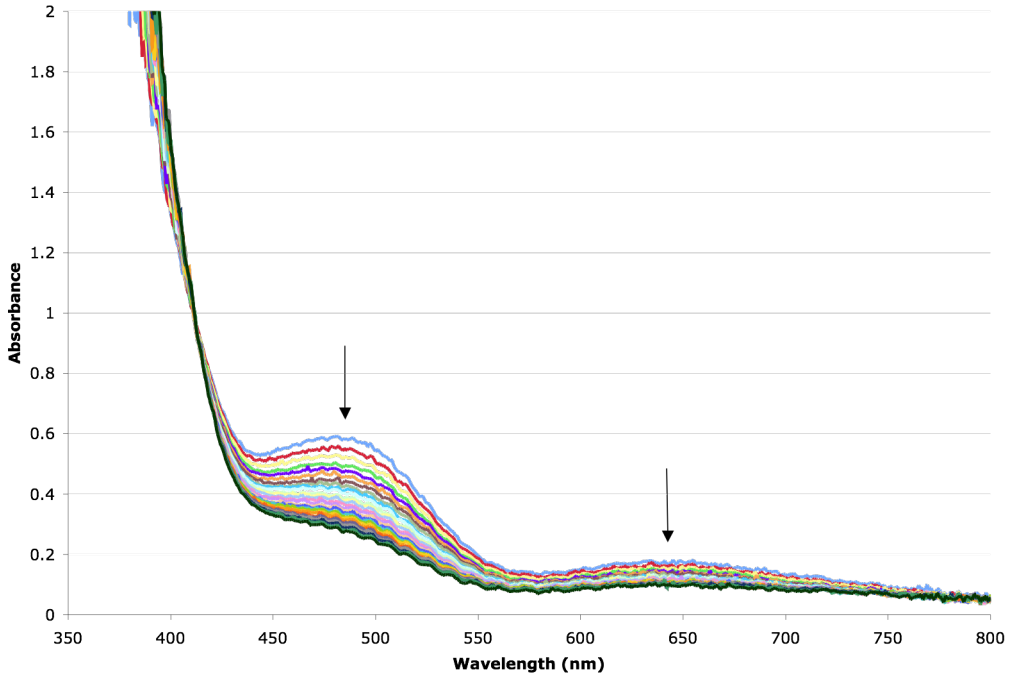


Figure S39. UV-Vis spectrum of reaction of **5** (0.203 mM) with DBU-H^+OTf^- (5 eq) in 3:2 toluene/acetonitrile at -40 °C. Scan interval: 20 minutes. Total reaction time: 6 hours.

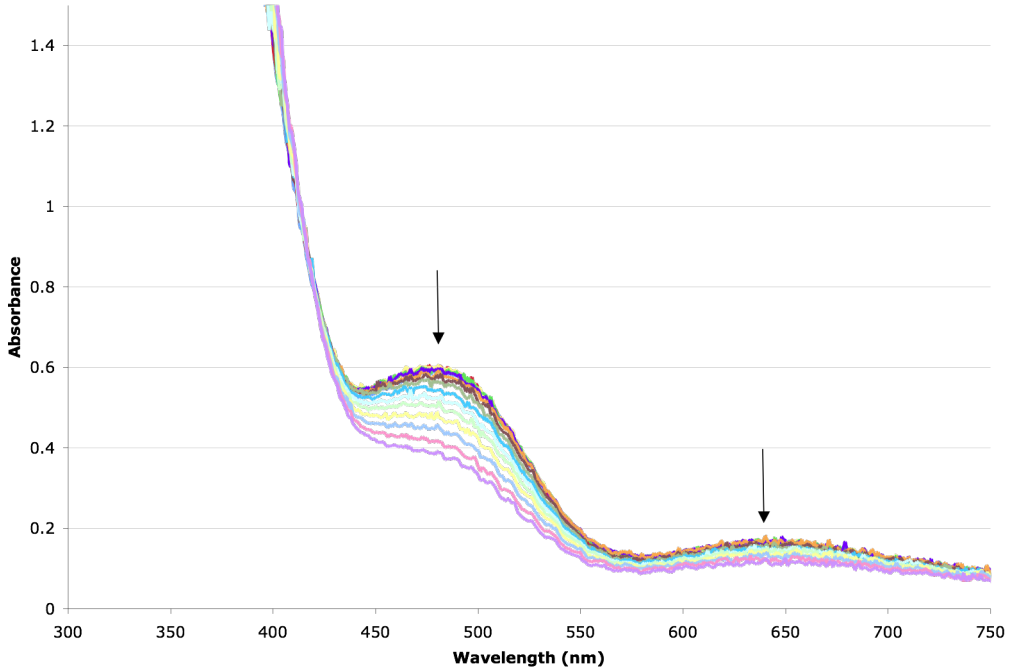


Figure S40. UV-Vis spectrum of reaction of **5** (0.203 mM) with pyrrole (5 eq) at -40 °C, in 3:2 toluene/acetonitrile. Scan interval: 20 minutes. Total reaction time 6 h.

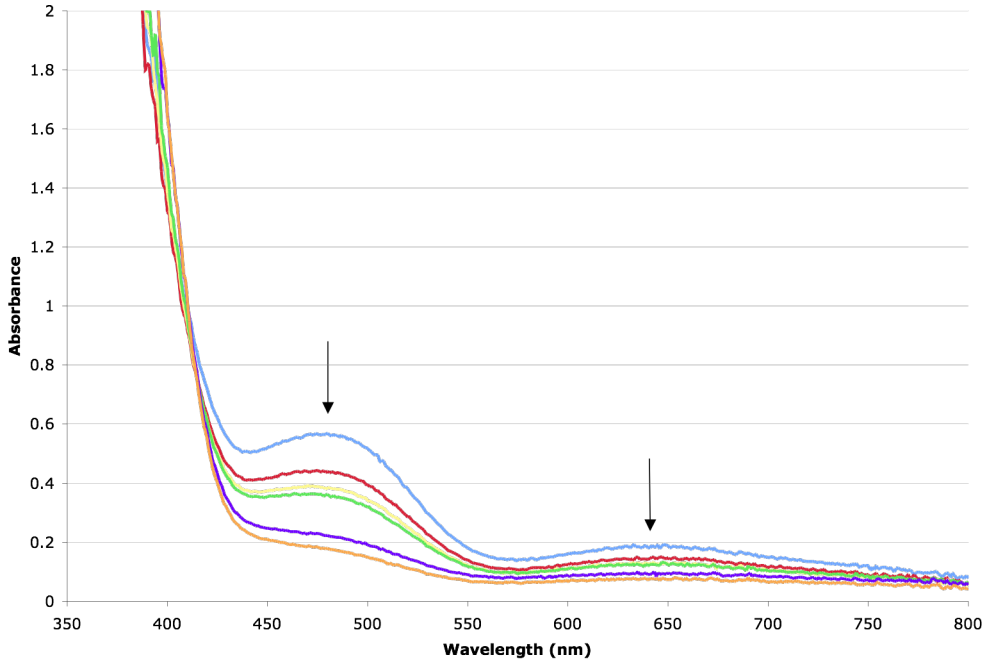


Figure S41. UV-Vis spectrum of reaction of 5 (0.126 mM) with TEMPO-H in propionitrile at -78 °C. Scan interval: 30 minutes. Total reaction time: 4 hours.

EPR spectra

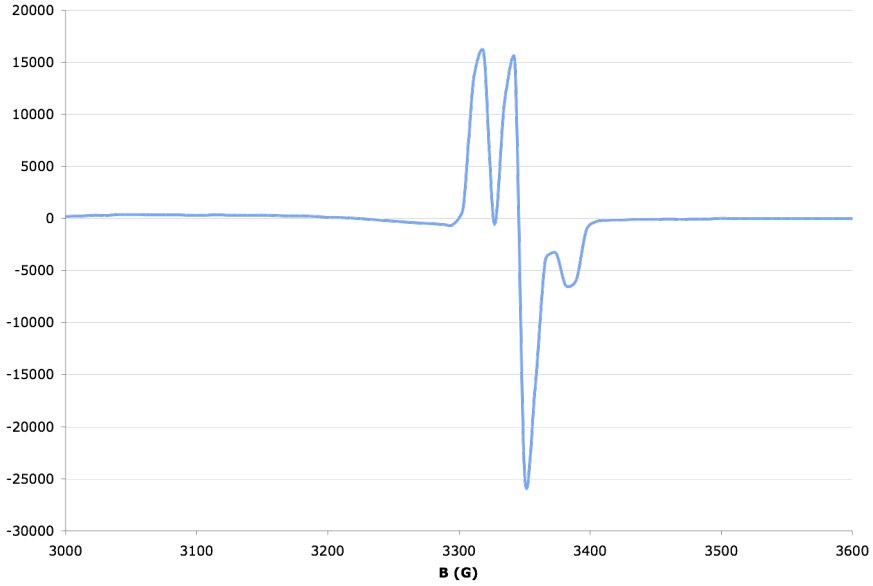


Figure S42. EPR spectrum of reaction of **5** (0.27mM) with 30 eq TEMPO-H in 3:2 toluene/acetonitrile at 77K. Frequency: 9.374 GHz. Power: 0.644mW.

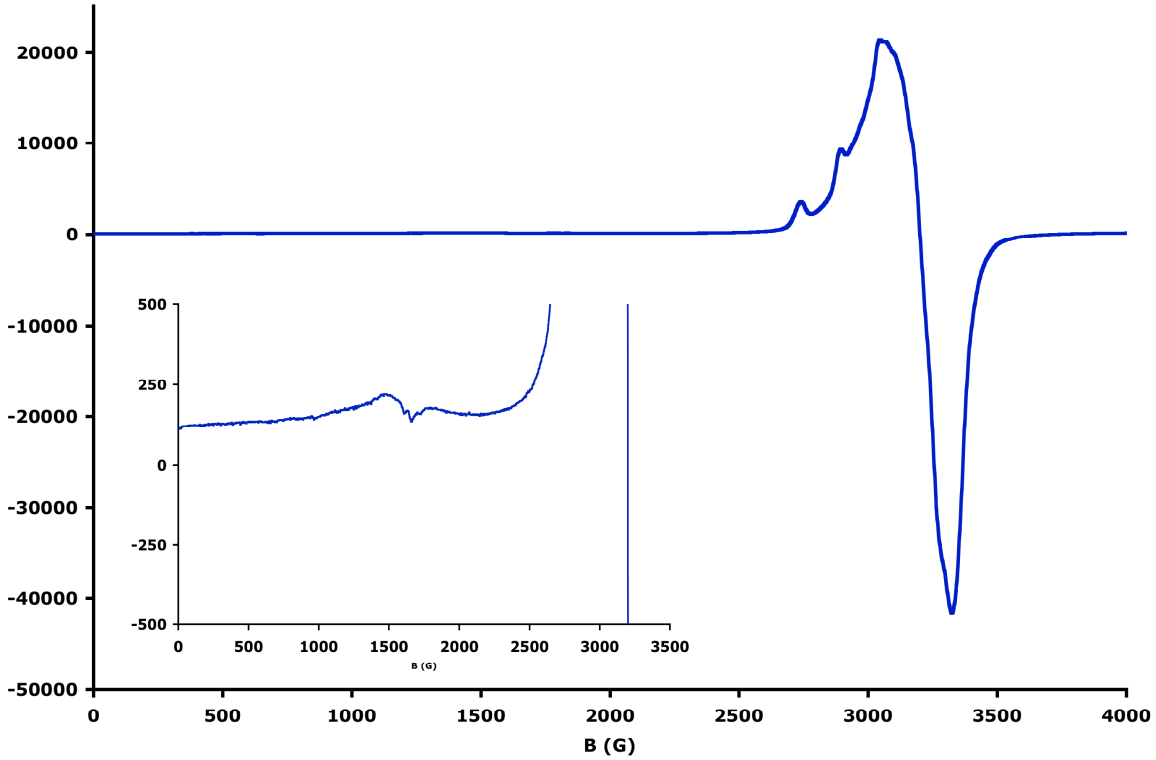


Figure S43. EPR spectrum of **5** (20mM) in 1:1 propionitrile/toluene at 15 K. The inset displays an enlarged view of the g~4 region. Frequency: 9.374 GHz. Power: 0.644mW.

*Crystallographic Information for complex **4***

General considerations

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 846679.

Table S2. Crystal and refinement data for 4

Empirical formula	$[C_{75}H_{81}N_{16}O_3Cu_3Y]^{3+}$ (see Details)
Formula weight	1534.09
Crystallization Solvent	Acetonitrile/diethyl ether
Crystal Habit	Blade
Crystal size	0.40 x 0.36 x 0.12 mm^3
Crystal color	Yellow
Type of diffractometer	Bruker KAPPA APEX II
Wavelength	0.71073 Å MoKa
Data Collection Temperature	100(2) K
q range for 9751 reflections used	

in lattice determination	2.33 to 24.61°	
Unit cell dimensions	a = 14.2953(5) Å	a= 75.534(2)°
	b = 18.3037(7) Å	b= 71.127(2)°
	c = 20.8565(8) Å	g = 74.087(2)°
Volume	4887.5(3) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.042 Mg/m^3	
F(000)	1586	
Data collection program	Bruker APEX2 v2009.7-0	
q range for data collection	2.09 to 26.58°	
Completeness to q = 26.58°	98.7 %	
Index ranges	$-17 \le h \le 17, -22 \le k \le 23, -26 \le l \le 26$	
Data collection scan type	ω scans; 14 settings	
Data reduction program	Bruker SAINT-Plus v7.68A	
Reflections collected	135224	
Independent reflections	20138 [R_{int}= 0.0637]	
Absorption coefficient	1.275 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.6174	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Primary solution method	Direct methods	
Secondary solution method	Difference Fourier map	
Hydrogen placement	Geometric positions	
Structure refinement program	SHELXL-97 (Sheldrick, 2008)	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	20138 / 13 / 893	
Treatment of hydrogen atoms	Riding	
Goodness-of-fit on F^2	3.264	
Final R indices [I>2s(I), 13445 reflections]	R1 = 0.0700, *w*R2 = 0.0973	
R indices (all data)	R1 = 0.1002, *w*R2 = 0.0983	
Type of weighting scheme used	Sigma	
Weighting scheme used	$w=1/s^2(Fo^2)$	
Max shift/error	0.000	
Average shift/error	0.000	

Largest diff. peak and hole	1.514 and -1.134 e.Å^{-3}

Special refinement details for 4

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. The solvent region of the crystal is very disordered, including the triflate anions. The intensities were adjusted such that the solvent region was flattened in the electron density map using SQUEEZE,[7] with the triflate anions, although being clearly present, being excluded from the final model. The volume of the solvent region is 1891Å^3. approximately 39% of the total volume. A total of 514 electrons were accounted for which is reasonable agreement for three triflate and three acetonitrile molecules per asymmetric unit. Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

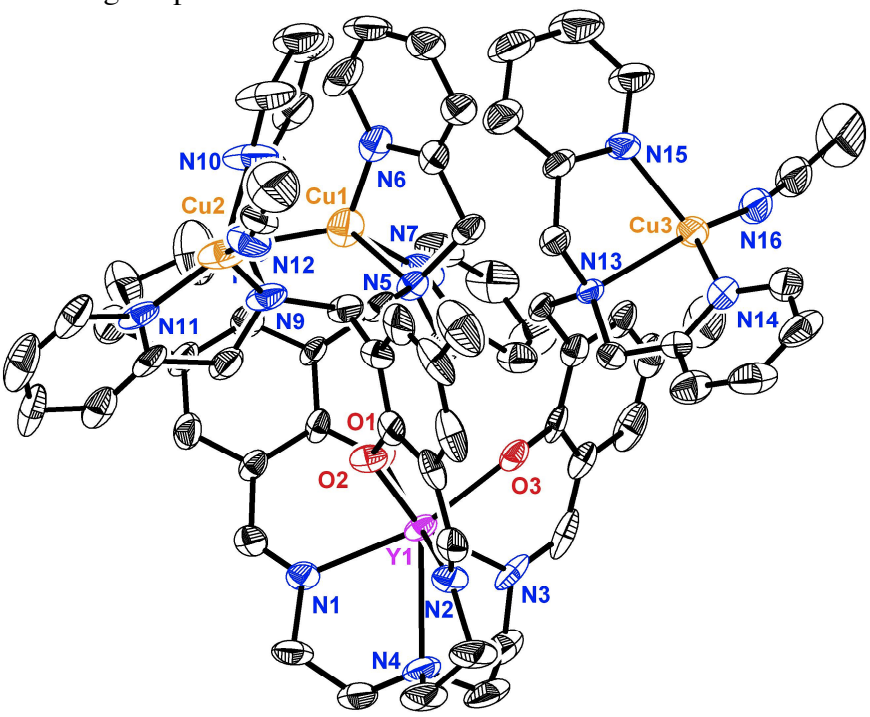


Figure S44. Structural drawing of **4** with 50% thermal ellipsoids. View perpendicular to Y1-N4 bond

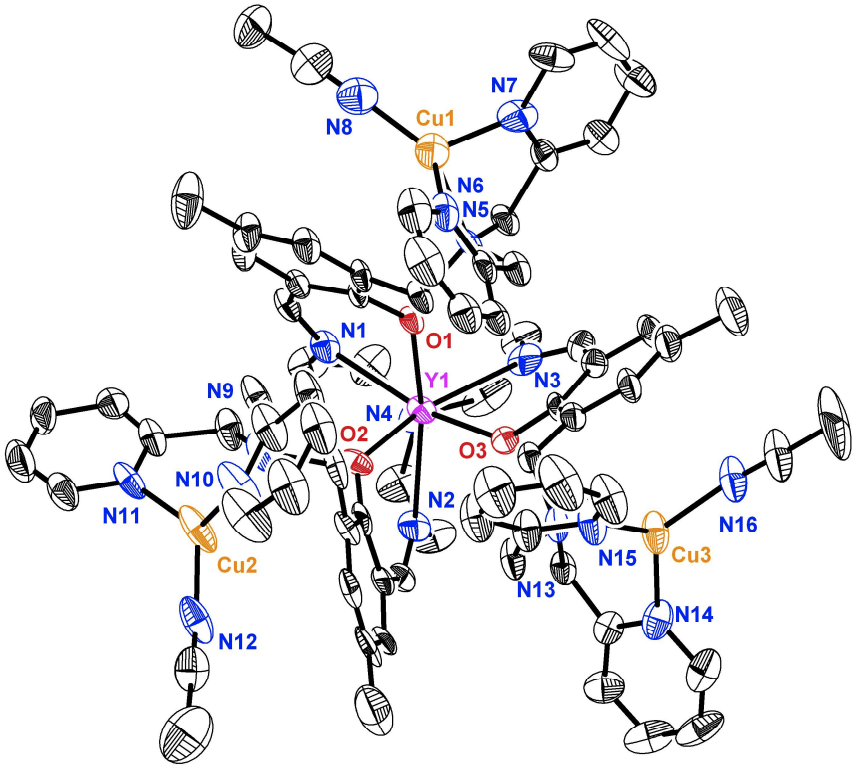


Figure S45. Structural drawing of **4** with 50% thermal ellipsoids. View along the Y1-N4 bond from the top of the molecule.

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4**. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Y(1)	2621(1)	-125(1)	3382(1)	30(1)
Cu(1)	3134(1)	1840(1)	-236(1)	53(1)
Cu(2)	-1948(1)	2936(1)	3381(1)	60(1)
Cu(3)	4337(1)	3582(1)	2909(1)	47(1)
O(1)	2706(2)	214(2)	2286(1)	29(1)
O(2)	1229(2)	735(2)	3584(1)	34(1)
O(3)	3402(2)	809(2)	3248(1)	33(1)
N(1)	1744(3)	-963(2)	3136(2)	37(1)
N(2)	2091(3)	-165(2)	4636(2)	38(1)
N(3)	4456(3)	-696(2)	3055(2)	44(1)
N(4)	2992(3)	-1536(2)	4067(2)	46(1)
N(5)	3371(2)	1665(2)	786(2)	30(1)
N(6)	2739(3)	2953(2)	-96(2)	47(1)
N(7)	4635(3)	1328(2)	-421(2)	51(1)

N(8)	2417(4)	1381(3)	-577(2)	60(1)
N(9)	-517(3)	2242(2)	2844(2)	47(1)
N(10)	-1463(3)	3779(2)	2546(2)	70(2)
N(11)	-2465(3)	2058(2)	3297(2)	42(1)
N(12)	-2469(3)	3448(2)	4117(3)	57(2)
N(13)	3191(2)	2863(2)	3193(2)	32(1)
N(14)	4118(3)	3331(2)	3943(2)	47(1)
N(15)	3243(3)	4348(2)	2487(2)	50(1)
N(16)	5608(3)	3689(2)	2260(2)	55(1)
C(1)	1664(4)	-1679(2)	3642(2)	46(1)
C(2)	2652(4)	-2052(3)	3799(3)	54(2)
C(3)	2527(4)	-865(3)	5047(2)	57(2)
C(4)	2465(4)	-1543(3)	4805(2)	59(2)
C(5)	4738(4)	-1539(3)	3221(3)	54(2)
C(6)	4110(4)	-1789(3)	3960(3)	64(2)
C(7)	1320(3)	-812(2)	2647(2)	37(1)
C(8)	1332(3)	-125(2)	2111(2)	31(1)
C(9)	643(3)	37(3)	1723(2)	44(1)
C(10)	559(4)	682(3)	1229(2)	48(1)
C(11)	1195(3)	1178(3)	1119(2)	44(1)
C(12)	1901(3)	1044(2)	1470(2)	31(1)
C(13)	2002(3)	368(3)	1969(2)	30(1)
C(14)	-223(4)	852(3)	843(3)	79(2)
C(15)	2479(3)	1637(2)	1400(2)	36(1)
C(16)	3730(3)	2381(2)	722(2)	39(1)
C(17)	3065(3)	3078(3)	408(2)	37(1)
C(18)	2804(3)	3781(3)	622(2)	42(1)
C(19)	2203(4)	4401(3)	316(3)	51(2)
C(20)	1854(4)	4300(3)	-174(3)	64(2)
C(21)	2119(4)	3595(4)	-382(3)	67(2)
C(22)	4174(3)	994(3)	834(2)	38(1)
C(23)	4981(3)	969(2)	139(2)	36(1)
C(24)	5966(4)	613(3)	84(3)	45(1)
C(25)	6672(4)	606(3)	-557(3)	65(2)
C(26)	6314(4)	986(3)	-1116(3)	70(2)
C(27)	5341(4)	1327(3)	-1056(2)	54(2)
C(28)	1971(5)	1118(5)	-778(4)	97(3)
C(29A)	1244(14)	1262(13)	-1251(10)	161(9)
C(29B)	1439(7)	578(5)	-898(5)	75(3)
C(30)	1551(3)	385(3)	4939(2)	36(1)
C(31)	1034(3)	1142(3)	4644(2)	39(1)
C(32)	646(3)	1735(3)	5010(3)	53(2)
C(33)	168(4)	2487(3)	4742(3)	58(2)
C(34)	95(3)	2612(3)	4081(3)	50(2)
C(35)	445(3)	2052(3)	3698(2)	35(1)
C(36)	927(3)	1285(3)	3938(2)	36(1)

C(37)	-181(4)	3100(3)	5141(3)	93(2)
C(38)	458(3)	2246(3)	2952(2)	49(2)
C(39)	-516(4)	2609(3)	2118(2)	59(2)
C(40)	-710(4)	3456(3)	2043(3)	59(2)
C(41)	-169(4)	3923(3)	1474(3)	67(2)
C(42)	-407(4)	4716(3)	1463(3)	67(2)
C(43)	-1143(4)	5014(3)	1962(3)	78(2)
C(44)	-1690(4)	4520(3)	2508(3)	84(2)
C(45)	-671(3)	1445(3)	2982(2)	49(2)
C(46)	-1788(4)	1434(3)	3108(2)	43(1)
C(47)	-2025(4)	789(3)	3055(2)	49(2)
C(48)	-3044(4)	754(4)	3235(3)	62(2)
C(49)	-3740(5)	1404(5)	3436(3)	78(2)
C(50)	-3446(4)	2033(4)	3456(2)	58(2)
C(51)	-2846(5)	3870(3)	4450(3)	55(2)
C(52)	-3354(5)	4463(4)	4880(3)	115(3)
C(53)	5183(4)	-317(3)	2715(3)	54(2)
C(54)	5057(3)	515(3)	2519(2)	37(1)
C(55)	5902(4)	777(4)	2041(3)	57(2)
C(56)	5857(4)	1551(4)	1808(2)	53(2)
C(57)	4986(3)	2064(3)	2043(2)	42(1)
C(58)	4144(3)	1828(3)	2510(2)	34(1)
C(59)	4193(3)	1033(3)	2766(2)	33(1)
C(60)	6796(4)	1825(3)	1319(3)	82(2)
C(61)	3196(3)	2400(2)	2705(2)	30(1)
C(62)	3263(3)	2393(2)	3861(2)	35(1)
C(63)	3559(3)	2795(2)	4292(2)	36(1)
C(64)	3330(4)	2607(3)	5004(2)	50(1)
C(65)	3680(5)	2944(3)	5359(3)	62(2)
C(66)	4269(5)	3462(3)	5015(3)	65(2)
C(67)	4478(4)	3669(3)	4305(3)	55(2)
C(68)	2247(3)	3479(3)	3305(2)	44(1)
C(69)	2348(4)	4148(3)	2698(2)	45(1)
C(70)	1573(4)	4523(3)	2417(3)	63(2)
C(71)	1728(4)	5147(3)	1857(3)	73(2)
C(72)	2639(5)	5360(3)	1632(3)	84(2)
C(73)	3382(4)	4951(3)	1963(3)	64(2)
C(74)	6264(4)	3923(3)	1881(3)	70(2)
C(75)	7080(4)	4258(4)	1367(3)	140(3)

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for **4**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}

Y(1)	298(3)	347(3)	178(2)	59(2)	-75(2)	-23(2)
Cu(1)	542(5)	768(5)	262(3)	122(3)	-120(3)	-283(4)
Cu(2)	312(4)	529(4)	540(4)	250(3)	81(3)	33(3)
Cu(3)	345(4)	490(4)	507(4)	172(3)	-137(3)	-204(3)
O(1)	213(18)	427(19)	159(15)	49(13)	-31(14)	-77(14)
O(2)	370(20)	350(19)	177(16)	12(14)	8(14)	-44(15)
O(3)	296(19)	470(20)	195(16)	18(14)	-119(15)	-68(15)
N(1)	360(30)	410(20)	250(20)	99(18)	-56(19)	-142(19)
N(2)	450(30)	410(30)	200(20)	103(19)	-50(19)	-160(20)
N(3)	410(30)	510(30)	450(30)	-130(20)	-320(20)	150(20)
N(4)	690(30)	300(20)	450(30)	50(20)	-370(20)	-30(20)
N(5)	220(20)	420(20)	155(19)	57(17)	13(17)	-66(19)
N(6)	370(30)	700(30)	290(20)	170(20)	-100(20)	-240(20)
N(7)	760(30)	530(30)	210(20)	90(20)	-50(20)	-330(20)
N(8)	690(40)	600(30)	470(30)	-20(20)	-150(30)	-160(30)
N(9)	360(30)	460(30)	390(20)	200(20)	-70(20)	-50(20)
N(10)	450(30)	430(30)	710(30)	290(30)	100(30)	60(20)
N(11)	220(30)	510(30)	270(20)	170(19)	2(19)	50(20)
N(12)	290(30)	310(30)	850(40)	0(30)	40(30)	0(20)
N(13)	240(20)	310(20)	360(20)	130(18)	-134(19)	-91(18)
N(14)	460(30)	410(30)	570(30)	30(20)	-290(20)	-110(20)
N(15)	370(30)	440(30)	580(30)	250(20)	-160(20)	-180(20)
N(16)	350(30)	650(30)	580(30)	180(20)	-160(20)	-210(20)
C(1)	730(40)	270(30)	380(30)	90(20)	-210(30)	-140(30)
C(2)	750(40)	330(30)	560(40)	120(30)	-370(30)	-120(30)
C(3)	990(50)	430(30)	260(30)	150(20)	-270(30)	-200(30)
C(4)	940(50)	480(30)	310(30)	200(30)	-290(30)	-190(30)
C(5)	610(40)	420(30)	640(40)	-160(30)	-390(30)	130(30)
C(6)	1050(50)	220(30)	790(40)	-130(30)	-670(40)	160(30)
C(7)	240(30)	410(30)	330(30)	20(20)	30(20)	-110(20)
C(8)	200(30)	450(30)	230(30)	20(20)	-50(20)	-40(20)
C(9)	290(30)	580(30)	450(30)	60(30)	-140(30)	-180(30)
C(10)	370(30)	660(40)	380(30)	160(30)	-240(30)	-150(30)
C(11)	350(30)	590(30)	290(30)	150(20)	-70(20)	-200(30)
C(12)	160(30)	450(30)	250(30)	100(20)	-70(20)	-70(20)
C(13)	180(30)	500(30)	180(20)	20(20)	-30(20)	-130(20)
C(14)	670(40)	900(50)	850(50)	380(40)	-480(40)	-420(40)
C(15)	210(30)	530(30)	180(20)	150(20)	-20(20)	-70(20)
C(16)	290(30)	520(30)	260(30)	110(20)	-80(20)	-100(20)
C(17)	220(30)	550(40)	240(30)	80(20)	10(20)	-160(30)
C(18)	340(30)	480(30)	340(30)	80(30)	-20(20)	-130(30)
C(19)	450(40)	510(40)	450(30)	110(30)	-60(30)	-160(30)
C(20)	550(40)	360(40)	710(40)	270(30)	-100(30)	-70(30)
C(21)	500(40)	1020(50)	360(30)	330(30)	-220(30)	-240(40)

C(22)	300(30)	560(30)	210(30)	50(20)	10(20)	-150(30)
C(23)	300(30)	340(30)	380(30)	-20(20)	-10(20)	-130(20)
C(24)	440(40)	340(30)	480(30)	-30(20)	-70(30)	-30(30)
C(25)	470(40)	770(40)	440(40)	10(30)	20(30)	20(30)
C(26)	460(40)	670(40)	600(40)	-60(30)	230(30)	-40(30)
C(27)	770(50)	410(30)	290(30)	-40(20)	30(30)	-140(30)
C(28)	820(60)	1330(70)	960(60)	-560(50)	-110(50)	-380(50)
C(29A)	1640(100)	1590(100)	1650(100)	-250(50)	-460(50)	-440(50)
C(29B)	760(50)	760(50)	920(50)	-260(40)	-250(40)	-330(40)
C(30)	310(30)	500(30)	240(30)	-10(20)	20(20)	-200(30)
C(31)	270(30)	560(30)	340(30)	-120(30)	120(20)	-290(30)
C(32)	270(30)	830(50)	530(40)	-410(30)	220(30)	-310(30)
C(33)	180(30)	440(40)	1020(50)	-440(40)	270(30)	-140(30)
C(34)	190(30)	640(40)	610(40)	-80(30)	50(30)	-190(30)
C(35)	170(30)	300(30)	430(30)	-30(20)	70(20)	-40(20)
C(36)	180(30)	510(30)	320(30)	40(30)	30(20)	-200(20)
C(37)	530(40)	800(50)	1390(60)	-490(50)	140(40)	-250(40)
C(38)	150(30)	460(30)	640(40)	230(30)	-50(30)	-70(20)
C(39)	270(30)	750(40)	460(30)	260(30)	-10(30)	-80(30)
C(40)	360(40)	550(40)	560(40)	290(30)	-90(30)	-10(30)
C(41)	310(30)	950(50)	490(30)	380(30)	-90(30)	-210(30)
C(42)	430(40)	730(40)	580(40)	400(30)	-170(30)	-120(30)
C(43)	570(40)	630(40)	820(50)	370(40)	-160(40)	-110(30)
C(44)	630(40)	590(40)	780(50)	310(30)	-10(30)	110(30)
C(45)	280(30)	570(40)	490(30)	140(30)	-160(30)	-70(30)
C(46)	260(30)	700(40)	190(30)	250(30)	-90(20)	-120(30)
C(47)	400(40)	810(40)	210(30)	10(30)	-120(30)	-120(30)
C(48)	330(40)	1200(60)	390(30)	-50(30)	-170(30)	-250(40)
C(49)	280(40)	1480(70)	530(40)	-130(40)	-100(30)	-160(50)
C(50)	270(40)	970(50)	350(30)	30(30)	-100(30)	-20(30)
C(51)	550(50)	300(40)	800(50)	30(30)	-230(40)	-140(30)
C(52)	1420(70)	930(60)	1320(70)	-50(50)	-660(60)	-370(50)
C(53)	270(30)	980(50)	440(30)	-250(30)	-230(30)	10(30)
C(54)	220(30)	530(30)	360(30)	-140(30)	-130(20)	50(30)
C(55)	200(30)	990(50)	450(30)	-200(30)	-60(30)	20(30)
C(56)	340(40)	890(50)	360(30)	10(30)	-80(30)	-260(30)
C(57)	200(30)	660(40)	340(30)	20(30)	-70(20)	-90(30)
C(58)	280(30)	520(30)	190(20)	40(20)	-70(20)	-140(20)
C(59)	140(30)	630(30)	220(30)	-30(20)	-70(20)	-80(20)
C(60)	330(40)	1200(50)	750(40)	-30(40)	-10(30)	-200(40)
C(61)	240(30)	400(30)	240(20)	60(20)	-100(20)	-90(20)
C(62)	300(30)	400(30)	290(30)	110(20)	-70(20)	-170(20)
C(63)	400(30)	280(30)	400(30)	20(20)	-180(30)	-80(20)
C(64)	640(40)	450(30)	370(30)	-20(30)	-190(30)	-50(30)
C(65)	1030(50)	340(30)	510(40)	-80(30)	-380(40)	20(30)
C(66)	960(50)	440(40)	730(50)	-230(30)	-630(40)	160(30)

C(67)	580(40)	310(30)	880(50)	-100(30)	-410(40)	-30(30)
C(68)	280(30)	500(30)	470(30)	160(30)	-130(20)	-160(30)
C(69)	340(30)	430(30)	530(30)	140(30)	-230(30)	-60(30)
C(70)	420(40)	550(40)	800(40)	120(30)	-240(30)	-40(30)
C(71)	590(40)	600(40)	810(50)	200(30)	-310(40)	40(30)
C(72)	620(50)	660(40)	820(50)	350(30)	-60(40)	-90(40)
C(73)	440(40)	540(40)	680(40)	260(30)	-110(30)	-80(30)
C(74)	370(40)	870(50)	740(40)	270(40)	-200(30)	-270(30)
C(75)	570(50)	2170(90)	1130(60)	650(60)	-60(40)	-850(50)

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